Fabrication And Characterization Of 2D Reduced Graphene Oxide For Photocatalytic Activity

SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

M.Phil Chemistry

By

JAVED IQBAL

SU92-MSCHW-F22-026

Session: 2022-2024

Faculty of Sciences

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Supervisor Name: Dr. Fizza Naseem
Designation: Assistant Professor

Signature: ___________________________________

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This is to certify that the research work presented in this thesis, titled **"Fabrication and characterization of 2D reduced graphene oxide for photocatalytic activity"** was conducted by **"Javed Iqbal"** under the supervision of **"Dr. Fizza Naseem"**

No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of "**Chemistry"** in Faculty of Sciences at The Superior University, Lahore.

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a) External Examiner: Signature:_______________

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e) Name of Dean: Prof. Dr. Mohammad Naveed Babur Signature:_______________

f) Controller Examination: Dr. Muhammad Haris Signature:_______________

Dedication

This thesis is dedicated to my respected supervisor, **Dr. Fizza Naseem**, whose guidance, expertise, and unwavering support have been instrumental throughout this research journey. Her encouragement and insightful feedback consistently inspired me to strive for excellence.

I also dedicate this work to my beloved family, whose love, prayers, and constant encouragement have been the foundation of my strength. To my friends and colleagues, thank you for your support and companionship along the way.

Acknowledgments

In The Name of Allah, The Merciful, The Compassionate

I am extremely thankful to Almighty ‘Allah’ Who is the entire source of knowledge and wisdom endowed to mankind, for providing me with the acumen and vision to complete this endeavor.

I would like to express my profound gratitude to my supervisor for his/her wise counsel and encouraging attitude towards this study. I am extremely grateful to him/her for immensely facilitating me during my study period by ensuring the provision of favorable circumstances and conducive environment. This project would not have been possible without his support and expert guidance.

In the end, I would like to extend my deepest gratitude to my family members. Without their encouragement, I would not have been able to complete this endeavor. (You can always choose your own wordings; this is only a format/ sample to be followed for uniformity of all thesis).

Javed Iqbal

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List of Abbreviations

XrGO	Exfoliated reduced graphene oxide
TiO_2	Titanium oxide
EDX	Energy-Dispersive X-ray Analysis
ZnO	Zinc oxide
NO_2	Nitrogen Dioxide
N_2O_4	Dinitrogen tetraoxide
DNA	Deoxyribonucleic acid
CO	Carbon monoxide
C=O	Carbonyl group
O-H	Hydroxide
LbL	Layer-by-Layer
Ag^+	Silver ion
$KMnO_4$	Potassium permanganate
$NaNO_3$	Sodium nitrate
H_2SO_4	Sulfuric acid
H_2O_2	Hydrogen peroxide
HCl	Hydrochloric acid
DI	Deionized water
XGO	Exfoliated graphene oxide
GC-FID	Gas Chromatography-Flame Ionization Detector
CH_4	Methane
H_2	Hydrogen gas
PL	Photoluminescence
CuO	Copper (II) oxide

ABSTRACT

The increase in atmospheric carbon dioxide (CO_2) concentrations has raised serious societal concerns due to its effect on global warming. As a sustainable method of energy generation, it would be ideal to be able to capture the CO_2 on a massive scale and incorporate it back into the utilization cycle. In fact, using only sunlight is necessary for the generation of fuels from CO_2 to have a positive energy balance. Low photoresponse to visible light is the issue with the great majority of photocatalysts, which leads to low photoconversion efficiency. Redox reaction of CO_2 and H_2O with photocatalysts such as XrGO and rGO to produce solar fuels is a promising approach in reducing the environmental impacts of greenhouse gasses. This thesis describes an in-depth synthesis of four photochemical catalysts and their photocatalytic conversion of CO_2 to methanol, thereby addressing the above-mentioned problems by applying synthesised nano-based catalysts. Prior to photocatalytic reduction studies, catalysts such as GO, XrGO, rGO, and XGO were synthesized and characterized using various spectroscopic and imaging techniques such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray Photoelectron Spectroscopy (XPS), Energy-Dispersive X-ray Spectroscopy (EDX), Photoluminescence (PL) and UV-visible spectroscopy (UV-Vis). The conversion yield of CO_2 to methanol on GO, XrGO, rGO and XGO reached 0.101 mmol/gh, 0.26 mmol/gh, 0.143 mmol/gh and 0.053 mmol/gh, respectively, after 4 h of irradiation. Exfoliation of graphene oxide results in 2D sheets which cause in increase in surface area due to this CO_2 absorption increase and photocatalytic activity enhance. GC-FID was used to measure the product's formation, which eventually illustrates selectivity for a specific product. The research will deepen the understanding that XrGO based photocatalyst show higher activity and provide new ideas for designing efficient photocatalysts.

CHAPTER 1

INTRODUCTION

1.1 An overview of graphene and graphene oxide.

1.1.1 Graphene

The prefix "graph" for graphite and the suffix "-ene" for the C-C double bond merge to form the name graphene. Boehm et al. recommended the term graphene in 1986, and it purely refers to single carbon layer. The International later formalized this word. IUPAC, the Union for Pure and Applied Chemistry. Afterwards, belongs to a single carbon layer of graphite in the definition of graphene structure, utilizing an analogy to describe the nature of polycyclic aromatic nearly infinite-sized hydrocarbons. Moreover, graphene is recognized as the progenitor of all allotropes of carbon. Rolling out graphene (2D) turn a one-dimensional carbon nanotubes (1D), however if a graphene is being when wrapped, a fullerene will develop (0D) and separate into sheets of graphite (3D) (Figure 1.1) [1].

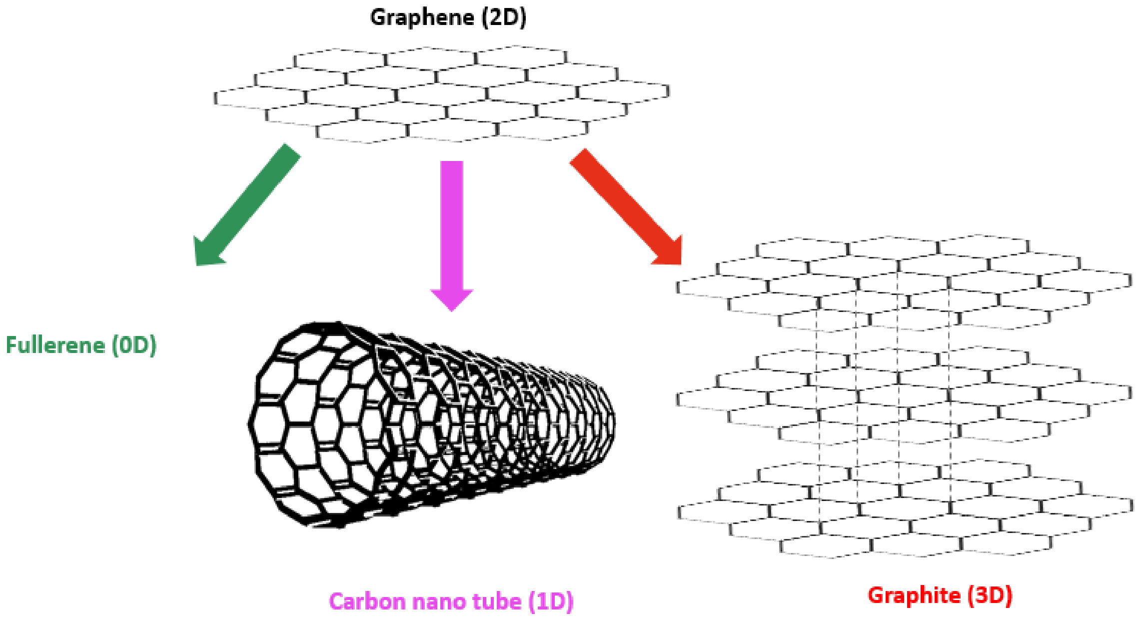


Figure 1.1 Graphene and related structures

From relative obscurity, graphene a one-atom thick layer made up of carbon atoms organized laterally in a hexagonal carbon lattice known as a "honeycomb" consisting of carbon atoms in sp^2 hybridization orbitals has emerged as an intriguing and promising framework for two-dimensional solids (Figure 1.2) [2].

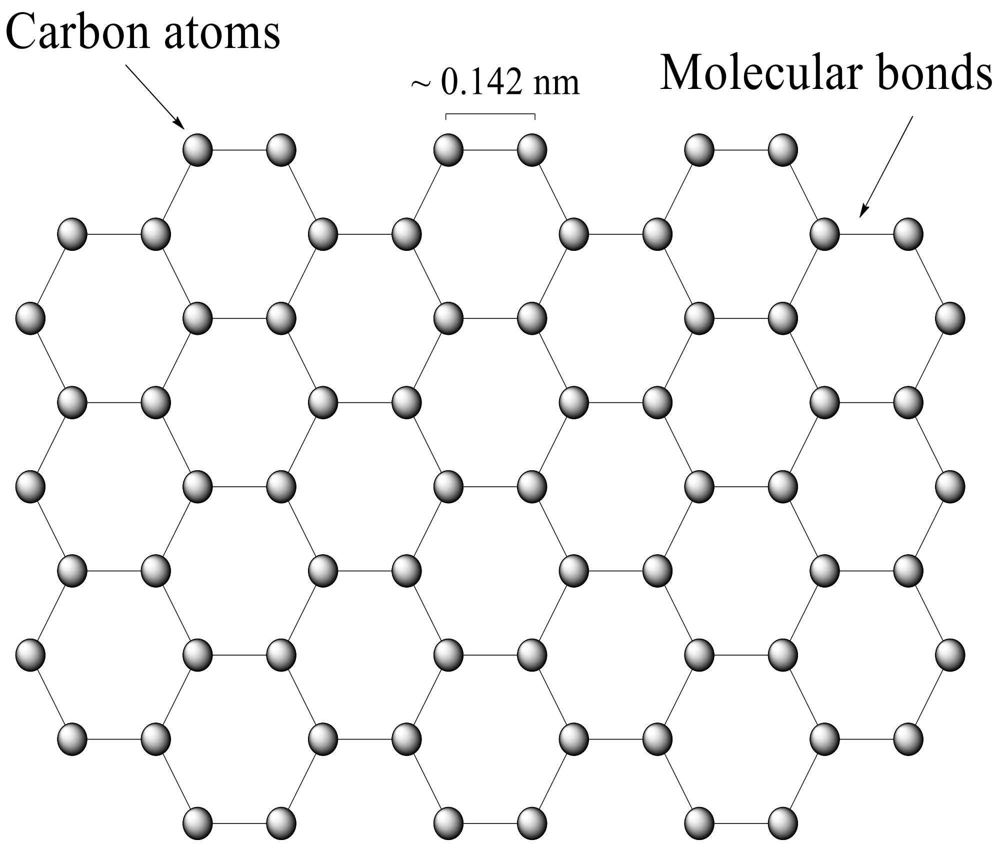


Figure 1.2 Schematic of the structure of a graphene sheet.

Due to its exceptional physicochemical qualities, including its high mechanical strength, high electron mobility, and large specific surface area, good electrical conductivity, graphene has been the subject of extensive research. More recently, graphene has attracted significant interest in the electronics sector[3]. Graphene is being extensively investigated as an integral part of composite materials with enhanced capabilities for many applications in energy, biomedicine, electronics, composites, and membranes [4]. Several methods, including chemical vapour deposition (CVD), micromechanical exfoliation of graphite, epitaxial growth, chemical intercalation, and reduction of graphene oxide (GO), have been used to synthesize graphene [5].

1.1.2 Graphene oxide

Graphene oxide (GO) is a type of graphene derivative with oxygen-containing functional groups, including hydroxyl, epoxy, or carboxyl groups, bonded to the basal plane and edges. These functional groups get introduced by oxidizing graphite, which is commonly done using methods such as the Hummers' method. The addition of these functional categories changes the characteristics of graphene, changing it to an extremely versatile material.

Structurally, GO retains graphene essential hexagonal lattice, with disturbances produced by its abundance of oxygen groups. These groups of function produce sp^3 hybridized atoms of carbon, breaking the sp^2 chain and creating defects in the structure. The breakdown of the π-conjugated structure causes GO to be electrically insulating or have significantly lower conductivity than pristine graphene [6]. However, these flaws and functional groups provide GO special features that are not found in pristine graphene.

One of the most important properties of GO is its great dispersion in water along with other solvents that are polar, which is due to the hydrophilic characteristics of the oxygen-containing groups. This makes GO easy to process and allows for the production of stable suspension and films that can be used in a variety of applications. Furthermore, the functional groups found on GO's surface can operate as reaction sites for additional chemical changes, allowing its features to be tailored to specific uses.

The distinctions among graphene and GO are notable. As graphene thrives in electric conductivity & mechanical strength, GO is chemically versatile and processable. The inclusion of functional groups made up of oxygen in GO reduces its conductivity but increases its chemical reactivity, which can be useful in some applications requiring functionalization [7]. GO offers multiple benefits to pristine graphene, especially with terms of chemical modification and material processing. Its capacity to produce stable aqueous dispersions makes it easier to make composite components, coatings, and films. These synthetic materials can be employed in a variety of programs, including water filtration, because GO's hydrophilic nature permits it to interact well with pollutants. Furthermore, the functional groups found on GO can be utilized to bind different molecules, tiny particles, or polymers, resulting in hybrid materials having enhanced characteristics for use in catalysis, sensing, and drug delivery applications [8]. These include graphene & graphene oxide are extraordinary material having distinct structures and features that make them appropriate for a wide range of applications. Graphene outstanding mechanical and electrical properties make it perfect for electronic devices, sensors, and storage of energy, while its chemical flexibility and processability allow for applications in composites, purification of water, and functional materials. Understanding the distinct qualities and potential for these materials is critical for developing their application in cutting-edge technology.

1.2 Reduced graphene oxide (rGO)

1.2.1 Definition and properties

Reduced graphene oxide (rGO) is a type of graphene oxide (GO) which has been chemically and thermally reduced to re-establish some of the properties of pure graphene. The reduction procedure involves the elimination of oxygen-containing groups with functions found on GO, which considerably increases the material's electric conductivity and durability, getting it closer to the qualities of pure graphene.

GO can be reduced to rGO via a variety of processes, including chemical, thermal, or electrochemical reduction. Chemical reduction usually requires the application of reducing chemicals like hydrazine, borohydride of sodium, or ascorbic acid, among others. Thermal reduction, on the other hand, is heating GO to high temperatures, typically in an inert atmosphere, in order to eliminate oxygen groups. The same action is achieved using electrochemical reduction, which uses an electric current. Each of these approaches has advantages and disadvantages, and the reduction process used can influence the final qualities of the rGO [9]. The reduction process restores rGO's electrical conductivity by partially re-establishing the π-conjugated structure, which is damaged in GO. Although rGO does not have the exact same degree of conductivity as pristine graphene, it outperforms it, making it appropriate for applications that require conductive materials. Mechanically, rGO outperforms GO in terms of strength and flexibility, albeit it may still contain flaws or residual groups of oxygen that influence its overall performance.

During the process of reduction, rGO preserves certain functional groups that contain oxygen, which may be useful in some applications. These leftover functional groups can serve as active sites for additional chemical modification, allowing rGO to be customized for specific applications. These groups may also improve rGO's dispersibility in different solvents, making it easier to incorporate in composites including coatings [10]

1.2.2 Problem statement

Pristine graphene cannot catalyze the photo catalysis because of inefficient band gap, higher recombination of charge carriers and low absorption capacity. So, 2D reduced graphene oxide based materials are highly effective due to their unique physiochemical properties, hydrophobic nature and featuring large surface area which makes a room for charge separation and to lowering the activation barrier for photocatalytic activity.

1.2.3 Importance of photocatalytic activity

Reduced graphene oxide (rGO) enhances the photocatalytic ability of composite materials utilized in environmental and energy-related uses. One of the most important benefits of rGO for photocatalysis is its capacity to increase the separating and transport of pairs of photo generated electrons and holes, hence increasing total photocatalytic efficiency.

In photocatalytic techniques, rGO is an efficient support material for photocatalysts with semiconductors like TiO_2 and ZnO. The extremely high electric conductivity of rGO allows for the quick transport of electrons through the semiconductor to rGO, lowering the recombining rate of electron-hole pairs. This effective charge separation extends the lifespan of charge carriers, boosting their chances of participating in photocatalytic events.

The process that operates in photocatalytic processes employing rGO typically consists of many phases. If a semiconductor photocatalyst consumes light with energy equivalent to or above its band gap, electrons are driven from the valence into the conduction band, producing holes in the band of valence [11]. These photo generated holes and electrons can then travel to the photo catalyst’s surface to participate in redox processes. But lacking an effective separation of charges mechanism, many holes and electrons combine again, lowering photocatalytic efficiency.

If rGO is merged with a semiconductor, it creates a conductive channel of electrons, permitting them to quickly travel away toward the semiconductors surface. This separation minimizes recombination rates while increasing the total number of holes and electrons accessible for photocatalytic processes. In addition, rGO's huge surface area provides greater activity sites for the absorption of molecules that react, boosting their ability to communicate with photo generated charge carriers.

In terms of decreasing CO_2-enhanced photocatalysts may convert CO_2 into useful fuels hydrocarbons including methanol, ethanol, and methane. The photocatalytic decrease in CO_2 is a potential method for reducing emissions of greenhouse gases while providing renewable fuel. The addition of rGO to these photocatalytic systems increases the effectiveness of the lowering method through providing improved separation of charges and more sites of activity for the reaction [12]. The leftover oxygen-containing groups of function in rGO may engage in the photocatalytic procedure by serving as adsorption sites for CO_2 molecule. These functional chains can promote a connection between CO_2 and photo generated electrons, hence boosted CO_2 reduction to hydrocarbons.

1.3 Fabrication methods of graphene oxide

1.3.1 Modified Hummer's method.

William S. Hummers & Richard E. Offerman created the Hummer method in 1958, and it is one of the most extensively used ways for synthesizing graphene oxide (GO). This is the process of oxidizing graphite powder with highly concentrated sulfuric acid, acetate of sodium, and potassium permanganate. The process of oxidation introduces functional groups containing oxygen in the graphite structure, comprising the hydroxyl group the epoxy, and carboxyl groups, which makes graphite exfoliate and obtain graphene oxide sheets. The Hummer process is simple, highly scalable, and efficient, which makes it a highly favorable method for GO production.

But the old Hummer process has a lot of drawbacks as well, like the use of toxic chemicals, the generation of toxic waste, and the relatively low quality of the resulting GO. Numerous modifications and improvements have been applied to solve these challenges [13] to enhance the efficiency and quality of GO synthesis. A significant change is the use of less toxic oxidizing agents. Some research have substituted the acid phosphoric for the sodium nitrate, hoping to decrease the formation in the reaction of toxic gasses such as NO_2 and N_2O_4. In addition, this transformation can enhance oxidation efficiency and result GO with fewer structural defects.

Another advantage is tuning of reaction parameters such as temperature, reaction time and the feed ratio. For example, higher reaction temperatures can facilitate oxidation processes and elevate GO yields. Nevertheless, the temperature should be well regulated not to promote excessive oxidation which can significantly damage the graphene structure. Likewise, such conditions allows enhancing quality of GO produced, since a higher oxidizing agent ratio generally gives higher degrees of oxidation.

1.3.2 Different synthesis techniques

As the modified Hummer process has been widely used to fabricate GO, various other synthetic processes are directed at the production of reduced graphene oxide (rGO). These methods include chemical vapor deposition (CVD), thermal reduction, and electrochemical reduction, all having advantages and limitations.

Both chemical vapor deposition (CVD) is an accustomed method of manufacturing high-quality graphene and rGO. Herein, a source of carbon, such as methane or acetylene, is disassembled at high temperatures with the use of a catalyst, usually a metal support. The next Carbon atoms then come to form a layer on the substrate that forms graphene layer. CVD gives graphene with great mechanical and electrical properties but it requires frequent equipment and precise regulation of the circumstances of reaction. Moreover, CVD is better for producing large surfaces of graphene films, while tiny rGO sheets [14]. The other usual method for preparing rGO is via thermal reduction. GO is carburized at high temperatures often in vacuum to reduce the oxygen containing groups of function. The cases of thermal reduction are not numerous, but this process looks rather simple and allows obtaining rGO with a high electrical conductivity. But, the external conditions that are needed can be detrimental to the structure of the graphene and lead to imperfections, and lowered mechanical properties.

Electrochemical reduction is one of the methods that can be used to synthesize rGO of high quality and minimal defect. In this process, GO is dispersed on an electrode and is subjected to an electricity that reduces the oxygen groups. The electrochemical reduction is not very difficult to perform under ambient conditions, and monitoring of the reduction process is also precise. But it normally takes longer than thermal loss and may require the use of specialized tools [15].

1.3.3 Advantages of modified Hummer's method

However, several synthesis strategies are available, the modified Hummer method has the following advantages which make it appropriate for synthesizing GO. An advantage of using this concept is that it is easy to expand and simple. The modifications put forward in the current study can be easily extended to large-scale production, making the Hummer process suitable for industrial use. In addition, the method does not require complex technology or conditions for a reaction to occur so that it may be used in most laboratories.

It is also an advantage to be able to produce GO with sufficiently adjustable parameters to serve as the desired response. The properties of resultant GO can thus be altered depending on the shift in the reaction conditions and purification process as it will be discussed later on. The extent of oxidation, the size of the sheets, and the type and number and density of the functional groups can all be controlled to optimize the utility of GO forms in various uses.

The modified Hummer approach also provides fairly good yield of GO; which can be subsequently converted to rGO by employing a number of reduction processes. This makes it a low cost way of preparing large quantity of GO for research and application in industries. Modified Hummer method is one of the most efficient and easily adjustable technology for synthesizing of graphene oxide and reduced graphene oxide. Although there are other synthesis processes such as Chemical Vapor Deposition, thermal reduction, electrochemical reduction, and several features distinguish the modified Hummer method for synthesis of GO, namely; scalability, ease of synthesis and tunable properties of the generated GO. These procedures of production, therefore, need to be well understood and fine-tuned for enhancing the production and application of 2D reduced graphene oxide in different sectors.

1.4 Applications of 2D reduced graphene oxide

1.4.1 Photocatalytic CO_2 reduction

The conversion of atmospheric carbon dioxide (CO_2) through photocatalytic reduction of graphene oxide (rGO) offers a way toward environmental problems solution as well as synthesis of pure compounds. An increase in the CO_2 concentration in the atmosphere edged by fossil fuel utilization and deforestation is the primary attributor of global warming. Hence, identifying ways on minimizing carbon dioxide (CO_2) emission is relevant for ecological responsibility and global temperature management interventions [16]. The photocatalytic removal of CO_2 is also controlled by reduced graphene oxide (rGO). Photocatalysis is that a chemical reaction occurs with a photocatalyst through the use of light energy. When rGO is used in conjunction with semiconductor photocatalysts such as Titanium Dioxide or Zinc Oxide, the photocatalytic process is greatly enhanced. The rGO is an idea material in this respect owning to its large surface area, high electrical conductivity and its ability to act as an electron acceptor.

The conversion of CO_2 into useful compounds utilizing rGO incorporated photo catalysts is of much research interest. It should be pointed out that CO_2 can be treated photo catalytically and converted into such interesting compounds as ethanol, methanol, hydrocarbons etc. These compounds are widely used in industry and can beonyms of fuels, betin tomorrow energy [17]. Ethanol or methanol, are valuable sustainable fuels and chemical raw materials. The creation of these alcoholic beverages from CO_2 not only helps to reduce greenhouse gas emissions, but it also provides a sustainable way to manufacture fuels for use in the energy and transportation sectors. Furthermore, the creation of compounds from less carbon dioxide is critical for producing essential building blocks for the petrochemical industry, which includes plastic bottles, solvents, or synthetic fibers.

There are three main steps involved in carbon dioxide reduction process

- Creation of charges by adsorption of light.

- Separation of the produced charges.
- Oxidation–reduction reactions at the surface of the catalyst.

The given photo catalyst exposed to photon energy which is much higher than their band gap, charges carries like holes and electrons will be synthesize in the conduction band and valance band. These electrons in the conduction band are responsible for the reduction of carbon dioxide and for conversion of that absorbed carbon dioxide to different by – products like carbon monoxide alcohol, carboxylic acid, methane etc.

Exfoliated reduced graphene oxide will be taken in photo reactor and carbon dioxide will be introduced with controlled flow rate. CO_2 will reduce in presence of water and photo catalyst. Efficiency of carbon dioxide reduction will be determined by using gas chromatography. Effect of different parameters like pH and temperature will also be determined to optimize the efficiency of photo catalyst.

1.4.2 Different potential applications

Apart from photocatalytic reduction of CO_2, 2D rGO can boast other applications such as energy strength and conversion, sensors and detecting technology, and material composites and coating.

1.4.3 Energy storage application and energy conversion

Graphene oxide has better electrical conductivity and larger surface area that make it a suitable material for energy storage instruments such as batteries and super capacitors. The rGO can be used in Lithium-ion batteries due to the way it can effectively host many lithium ions which increases the capacity and rate capability of the battery. In addition, the structure of rGO has the advantage of a large surface for storage of charges together with superior pathways for electron transport, leading to high power density as well as long cycle ability of the super capacitors. This suggests that rGO can be used in other energy conversion platforms such as fuel cells and solar cells as well. In fuel cells, rGO can have a catalytic support property, thus enhancing the effectiveness and durability of the catalytic materials used in electrochemical reaction. In preparation of solar panels, rGO can be incorporated into the layers of the photoactive materials or be a distinguishably evident conductive electrode enhancing the light trapping and charge transport capabilities [18].

1.4.4 Sensing and detection technology

The resulting material – reduced graphene oxide has some outstanding characteristic: its high surface area, and ability to conduct electric current or respond to changes in the atmosphere makes rGO a promising material for sensing. rGO is very sensitive and selective to the chemical or biological substances. For instance, rGO can be employed in gas sensors that aimed to detect poisonous gases such as ammonium, nitrogen oxide, and hydrogen sulfide in negligible concentrations [19]. Bio sensing employs rGO to differentiate analytes such as sugar, DNA or protein and used in medical detection, and environmental conditions. The high sensitivity of rGO-based sensors is attributable to the ability of the material and layer formed on or around it to amplify small changes in the environment around it to produce significant changes in electrical or optical signals that can be easily measured.

1.4.5 Composite products and coatings

Graphene oxide can enhance thermal, mechanical and electrical properties of composite materials, but reduction of graphene oxide may be useful to increase these properties. Incorporation of rGO with polymers, metals or ceramics improves the strength, hardness and electrical conductivity of the developed material. These enhanced characteristics give rGO based composite materials, their suitability in applications that include automobile, aerospace, construction and many others. When incorporated in coatings, rGO can offer the coatings attributes such as corrosion prevention, wear and thermal stability. For instance, rGO-based coats can be worn like coats on the metal surfaces in a bid to prevent oxidation and corrosion that are known to reduce the lifespan of such materials. In addition, rGO can also be used in electrical applications as a light, flexible, conductive layer for metal-based conductive coating.

1.5 Characterization methods

Characterization techniques play an essential role in evaluating the morphology, properties and functionalities of various materials including the 2D reduced graphene oxide. This section goes further exploring numerous methods applied for analysis of rGO and providing the data about its form, crystallography, optical properties, and elemental content.

1.5.1 Scanning electron microscope (SEM)

Scanning electron microscopy is a complex imaging technology used in investigating surface shape and functions of objects with great precision. SEM is a technique in which a focused beam of electrons scans the sample's surface with its signals being used to construct images. SEM stands out elements at the ability to generate linear on the scanned objects three-dimensional pictures within magnifications ranging between 10X to 100,000X depending on the equipment used [20].

SEM shows the 2D reduced shape and layer structure of graphene oxide (rGO), which is thin and semitransparent and commonly features folding and ruffling caused by the reduction and the presence of functional groups. SEM images can reveal the morphology, shape and distribution of rGO sheets and provide the information regarding the roughness and defects of the surface. SEM is also advantageous in studying the distribution or morphology of rGO and other elements in a composite or coatings. From SEM pictures, researchers can judge the blending of rGO with polymers or metals and how it changes the mechanical and electrical characteristics of the composite.

1.5.2 X-ray diffraction

X-ray Diffraction informally known as XRD is a technique that confirms the existence of crystal forms in materials and also the phase structure. XRD is an analytical technique in which a monochromatic X-ray beam is targeted to a sample material and the diffraction pattern produced is then recorded. The pattern is developed in X-ray diffraction from the crystal lattice of the material and offers details on the atomic arrangement as well as the crystalline states.

XRD may be employed to evaluate the level of graphitization of rGO and whether there are still crystalline phases that remain after the reduction from graphene oxide. GO generally exhibits a diffraction pattern, owing to its oxidized multilayered structure, while rGO has larger diffraction peaks caused by reduction-induced disorder, including defects.

The position of these peak and intensity of these peak in the XRD pattern give structural information regarding reduction process of GO to rGO and quality of rGO.

XRD characterization is especially important for assessing the crystallinity, or phase quality of rGO, which are perceived for electricity, strength, and heat conductivity features. Through comparing the obtained experimental XRD patterns with standard patterns, the researchers may recognize the crystalline phases in rGO and quantify the disorder imposed in the process of reduction.

1.5.3 UV-visible spectroscopy (UV-Vis)

UV-Vis spectroscopy is one of the methods in analysis of material optical properties and electronic transitions. UV-Vis spectroscopy is much similar to UV spectroscopy, because a ray of UV or visible light is passed through the sample and the amount of absorption of light transmittance can be recorded as a consequence of wavelength. This measurement provides details on the electronic transitions of the material including band gap energies, and conjugated π-electron systems [21].

UV-Vis spectroscopy is used to investigate the changes in light absorption properties of rGO due to the electronic transitions of π-π* bands within the structure of graphene. Specifically, for GO, it only had high UV absorption because of the presence of higher functional groups which include oxygen and, for rGO, it had higher visual absorption since it was lower in functional groups containing oxygen and had restored π-conjugated systems. The specific characteristics of rGO, namely band gap energy and the extent of π-conjugation could be resolved from its absorbance spectra and help understand its electrical conductivity as well as optical behavior. UV-vis spectroscopy also allows to quantitatively determine the concentration of rGO in solutions or thin films which is important for control of the processes and characterization of the material.

1.5.4 Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a procedure of identifying chemical bonds and the functioning groups in materials. FTIR spectroscopy comprises the transmission or absorption of infrared light through a material in relation to its frequencies. Different chemical bonds interact with infrared radiation in the region of some specific wavelengths, which leads to the formation of qualitatively different absorption bands that can be used for identification of functional groups and other structural characteristics. FTIR spectroscopy is particularly useful to identify oxygen-related functional groups that were not reduced with graphene oxide materials. This spectrum demonstrates that GO has considerable absorption bands corresponding to C=O, C-O and O-H stretching vibrations, which means it contains such functional groups as carboxyl, hydroxyl and epoxy and so on. On the other hand, rGO show a relatively less intensity of these bands, which suggest that reduction process also removes some of oxygen-containing molecules in some cases [22].

FTIR analysis provides both elemental and functional groups information of rGO's, which significantly contributes to understanding the stability, reactivity, and interfacial behavior of rGO s with other materials. Researchers may study efficiency of the method of reduction in order to produce rGO with desired properties, by comparing the FTIR spectrum of GO and rGO. Betters and characterizations include; SEM for morphology of the structure, XRD for structure of the resultant crystal, UV-vis and Fourier Transform Infrared Spectroscopy (FTIR) for the study of optical conducting behavior and chemical structural of 2D rGO respectively. These methods enhance understanding of rGO Structure-property relation and contribute to push this material to new applications in gadgets, energy storage, sensing, and composites.

1.6 Importance and objectives of the thesis

The research title "Fabrication and Characterization of 2D Reduced Graphene Oxide for Photocatalytic Activity" will aim at determining how the synthesized 2D rGO via modified Hummer process can be used in photocatalytic applications to improve environmental and industrial efficiency. This section presents the revenue generation relevance, goal, objective and expected results of the research.

1.7 Manufacturing high-quality 2D rGO with a modified Hummer's method:

Alterations to the general Hummer process are aimed at enhancing the reduction process, decreasing defects, and enhancing characterization of the material for practical applications. The produced material is fully analyzed using proper characterization techniques and the following techniques is used; scanning electron microscopy, X-Ray Diffraction, UV-visible Spectroscopy and Fourier Transform Infrared Spectroscopy.

These investigations will provide details on physical form, obtaining crystal structure, optical properties, and structure of synthesized rGO which can be useful for the understanding of its performance. One of the aims is to estimate the photocatalytic activity of the synthesized rGO to decrease CO_2 concentrations. CO photocatalytic reduction is under research as a green method of converting CO to useful products including ethanol, methanol, and hydrocarbon among others. The work therefore seeks to enhance the efficiency of these methods of conversion through the application of rGO properties as a photocatalyst [23].

AIMS AND OBJECTIVES

The objective of the present study is to synthesize the two dimension reduced graphene oxide for improved photocatalytic activity.

The objectives of this study are following below:

- Fabrication and characterization of 2D reduced graphene oxide.
- Exfoliation of graphene oxide.
- To determine photocatalytic activity by reduction of CO_2

CHAPTER 2

LITERATURE REVIEW

Graphene oxide (GO) has been the focus of tremendous interest as a result of the interest in its multidisciplinary uses including materials science, electronics, and biomedicine. Dreyer et al. (2010) selected and discussed the chemical property and functionalization of graphene oxide, because of its distinctive structure and activity. An extensive and commendable review of GO has been published by Dreyer et al. in 2010 and it covers everything ranging from the synthesis of this material, structure, chemical activity, and possible areas of application.

To this end, this paper stresses the need to consider the functionalization and reduction of GO particularly when modifying the material's properties for use in various applications. Possible directions for future studies proposed are the creation of new improved syntheses for GO, the investigation of other potential uses of GO in medicine, and the improvement of electric characteristics of GO for applications in electronics. This review also provides the starting point for the researchers who focus on the chemistry of graphene oxide and its application in various science and engineering domains [24].

The main and specific aim of the work by Stankovich et al was to investigate the use of graphene in polymer composites as a reinforcement material. The researchers wanted to study the effects of blending with graphene to improve mechanical electrical as well as thermal performance of these composites. This research arose from the abundant characteristics associated with graphene, including high mechanical strength, electrical conductive nature and large surface area that implied that the performance of composites could be enhanced through its addition.

After the appearance of this paper, much attention has been paid to graphene and its roles in composite materials. Further studies are aimed at the enhancement of the techniques for the synthesis of graphene and graphene oxide, enhancement of dispersion of graphene in polymeric matrices and development of novel applications of graphene reinforced polymeric composites. Research has been done that helped to clarify the interfacial behavior between graphene and the polymer matrix, and this has led to new improvements in properties of these two types of materials [25].

Before this current research, other materials for example synthetic polymers and the natural biopolymers have been used in pH dependent hydro gels. Nevertheless, the inclusion of graphene oxide added a completely new aspect in regards to the mechanical properties and potential applications of such films. Earlier research conducted on pH-sensitive hydrogels did not record the level of mechanical improvement as obtained after the addition of GO.

In the paper by Bai et al.(2011), the authors present the enhancement of pH sensitive hydrogels based on the addition of graphene oxide which is a substantial contribution to the existing literature. The synthesized composite hydrogel has potential in a number of real-life uses because of improved mechanical strength and pH sensitivity. Due to the remarkable features and possible usage of graphene related materials, the fabrication of graphene has recently attracted extensive interest. The formation of high-quality graphene is also known to require carefully controlling the reduction of graphene oxide (GO) [26].

A new approach for the reduction of graphene oxide with using hydroxylamine has been discussed by Zhou et al. in the work that was published in 2011.Atactic polymer containing carboxyl groups was also used in the synthesis of graphene oxide and for the reduction of graphene oxide the hydroxylamine was introduced by the current researchers. The methodology describe reductive process involving use of hydroxylamine to reduce graphene oxide at mild conditions. The reaction include the preparation of GO in water and the reaction with hydroxylamine hydrochloride and sodium hydroxide. The reagents are then mixed at room temperature under constant stirring for a considerable number of hours. This method is mentioned to be especially advantageous for its efficiency as compare to other reduction techniques.

Zhou et al. also contrast their method of using hydroxylamine for the reduction of palladium nanoparticles with that to other reducing agents notably hydrazine and sodium borohydride. Nonetheless, they observe that though these agents are efficient, the reaction conditions tend to be more demanding than with GO and the agent tends to introduce impurities or defects into the graphene structure. Hydroxylamine on the other hand is widely used because it offers a cleaner, high selectivity reduction process.

The authors here by Zhou et al. have provided a strong argument for the reduction of graphene oxide with hydroxylamine. The features that make their method distinct are ease, speed, and quality of graphene synthesized from this technique. The present work is relevant in the quest to provide solution to produce graphene at large scale for the advancement of other new technologies [27].

This sparked puberty in the graphene field, and the following work by Park and Ruoff in 2009 gives a synthetic chemist's perspective on the different synthetic approaches to graphene. The authors review different techniques to produce graphene with or without high volume production and the possible uses of each technique. This literature review will also aim at summarizing and passing an evaluation on the key points and contributions of their work.

Mentioned authors describe reduction techniques of GO, the provided outcomes are compared with the chemical and thermal methods.

- Different reducing agents and their effectiveness.
- The impact of reduction conditions on the quality of graphene.
- The trade-offs between achieving complete reduction and preserving the structural integrity of graphene.

Despite the fact that the current interest in graphene research is high, Park and Ruoff's paper published in 2009 provides a comprehensive and rather detailed overview of chemical approaches to graphene synthesis. The work done by these studies has led to a realization of many improvements in graphene synthesis, and its use in various technologies. It is noteworthy that even despite new tendencies in the development of the field, the presented principles and evaluations can be considered essential and useful [28].

Semiconductor and metal nanoparticles can be anchored on a two- dimensional carbon support, which makes Kamat (2010) to discuss the possibility of the broad applicability of graphene as a support material for the synthesis of hybrid materials. Carbon-based nanomaterial, known as graphene, nanoscale feature which is a single layer of carbon atoms packed in hexagonal lattice featuring high electrical conductivity, high surface area, mechanical strength and flexibility.

Such characteristics make it suitable for the use in supporting of various nanomaterials. Here, the author also points out that these properties can play a significant role in improving the performance and stability of the anchored nanoparticles. Hybrid materials Nano architectures have benefited from Kamat's (2010) work on developing and advancing the knowledge in graphene based system. When the semiconductor and metal nanoparticles are anchored to graphene, researchers have composite material with enhanced physical/chemical characteristics and application versatility. This review also elucidates that graphene, particularly a two-dimensional carbon support, must be considered for its valuable future contribution to differing technologies [29].

GO is considered a key material in nanotechnology materials since it possesses some essential properties and can be applied to several fields including electronic, energy, and bio science. Yang et al. (2009) in their paper describe the assignment aimed at studying the process of chemical transformations of graphene oxide films under thermal and chemical treatments. Chang et al uses X-ray photoelectron spectroscopy (XPS) and Micro Raman spectroscopy to fit into that gap, and investigate the changes in GO structure and chemical composition.

This research shows that GO can be effectively reduced by thermal as well as chemical treatments since both methods eliminate oxygen-containing functional species. However, the dynamics, and the results do not tally with each other. As observed, the thermal treatment is preferable in terms of the efficiency of rebuilding the graphitic structure, while the chemical reduction leads to the formation of new defects even though the total amount of oxygen decreases. These results are critical for tuning the characteristics of GO for certain applications where either higher reduction or the introduction of specific defects is necessary.

Yang et al. (2009) offer detailed description on how chemical and structural composition of GO films change with different treatments. The synergistic study of XPS and Micro-Raman techniques provides comprehensive insights into the reduction processes that remain critical when engineering GO-based materials for various applications. This work provides a foundation for future research regarding the functionalization and reduction of GO, and will greatly aid the enhancement of future applications involving graphene-based technologies [30].

The self-reduction synthesis of TiO_2-graphene nanocomposites also utilizes UV photocatalytic reduction process. Graphene oxide when in a colloidal suspension in water, is then dispersed with TiO_2 nanoparticles. UV light causes TiO_2 to produce electron-hole pairs where the electrons then reduce the GO to graphene. It is such a favorable method based on the simplification and the fact that reduction can be done at the ambient conditions with no use of chemical reducing agents.

The photocatalytic activity of the synthesized TiO_2-graphene nanocomposites was tested on the degradation of methylene blue (MB) under UV light source. This research reveals that the synthesized nanocomposites had notably improved photocatalytic properties over pristine TiO_2. This enhancement is as a result of increased charge separation and decreased recombination of the electron-hole pairs by the graphene sheets which doubles as electron acceptor and transporter.

Published by Williams, Seger, and Kamat, this work is a valuable contribution to the issue of nanocomposites that shows the application of TiO_2-graphene materials for improving photocatalytic effects. This is because the UV-assisted reduction method is a major innovation since it provides a sustainable way of preparing these composites. Further, more studies should be devoted to the development of the production process and identification of the possible areas of utilization of these nanocomposites [31].

This review aims to present the photocatalytic applications of selected two-dimensional carbon nanostructures, such as graphene oxide and reduced graphene oxide, for the treatment of wastewater. These materials have high oxygen functionalities, large surface area and effective adsorption sites. The review also looks into photocatalytic activity influences, the pH, initial dye concentration, quantity of photocatalyst, the charge on the composite surface [32].

Zhang et al. (2012) work on the utilization of GO as a matrix for enzyme immobilization is discussed in this paper. Immobilization of enzyme is a vital concept in biotechnology due to increased stability, reusability, and effectiveness in enzymes. This study concentrates on the use of GO because of the following characteristics: High specific surface area, biocompatibility and ability to be functionalized.

The present study by Zhang et al. (2012) further confirmed that graphene oxide has a vast potential of being used as a matrix for enzyme immobilization. The observations compare GO's performance to other similar materials, and indicate that it has the potential to be a valuable tool in a range of biotechnological applications because of its superior surface area, functionalization capacity, and stability. More studies and enhancement are required to overcome the distortions and to obtain the utmost advantage of GO in enzyme immobilization [33].

The synthesis of novel ZnO/ RGO (Reduced Graphene Oxide) nanocomposite photocatalysts has recently attracted considerable interest because of its higher photocatalytic efficiency in visible light. The incorporation of RGO into ZnO is expected to optimize the photocatalytic activity by factors such as increased charge carrier recombination, increased light absorption and improved electron conservation.

The interaction of RGO and ZnO in composite photolysis diversifies the structure and contributes to the improved visible light photocatalytic performance. These composites offer significant opportunities for numerous uses such as pollution control, generation of clean energy, and antimicrobial coatings. Further development of the synthesis methods, investigation of the molecular mechanisms and discovery of new potential uses are also desirable for the further development of these materials [34].

Raccichini et al have given a general account on the use of graphene in electrochemical energy storage. The objective of this paper is to explore the characteristics of graphene that can make it suitable to be used in energy storage like super capacitor, batteries among others. The investigation aims at identifying the methods of preparing graphene, and its structures, and measurements of performances. Raccichini et al. (2015) have also reported the updates and future direction with respect to the use of graphene for electrochemical energy storage applications. Despite this, the review points to enhanced application of graphene in energy storage technologies as well as the challenges that still needs innovations [35].

Graphene oxide is a functionalized derivative of graphene that has attracted substantial interest in view of its physiochemical properties and prospective uses in electronics, energy, and biomedicine. The process of the reduction of graphene oxide (rGO) is a very significant one in that it seeks to recover the electrical conductive and mechanical characteristics of graphene while at the same time, preserving selected of the modified functional groups that will increase it flexibility. A recent paper by Pei and Cheng (2012) regards the reduction of graphene oxide and it presents both, the methods and the mechanisms connected with the processes in question, as well as the current state of development within this field.

Another paper by Pei and Cheng (2012) gives a detailed analysis of graphical reduction of graphene oxide, the mechanisms involved and the properties of rGO. Thus, they described the current state and achievements in this field and the issues that remain to be solved. In the development of graphene-based structural applications, the anisotropic mechanical behavior of graphene sheet is well understood by the present work for targeted structural design and more advanced applications, see information reference [36].

Graphene oxide (GO) has attracted much interest sufficiently, because of its possessing such characteristics as the high surface area, conductivity and the ability to form stable aqueous dispersions. Choi et al. (2010) employ fabrication of optically transparent super capacitors employing a layer by layer (LbL) assembly technique using GO Nano sheets. To this end, this paper aims to evaluate the prospects and difficulties of employing high-performance energy storage devices into infrastructural see-through electronic usage.

Choi et al. (2010) contributed greatly of transparent electronics by showing the possibility of fabricating optically clear super capacitors utilizing LbL assembled GO Nano sheets. Hence, their work serves as a basis for subsequent studies related to the creation of transparent energy storage devices, disclosure of opportunities and difficulties in utilizing such technologies in practice [37].

Thakur and Karak (2012) in their paper describe a green synthesis of graphene oxide reduced by aqueous plant extracts. This green chemistry approach meets previously unaddressed objectives for environmentally friendly and less toxic approaches toward the reduction of GO, which is essential for creating graphene materials with lower levels of toxicity.

This has been supported by Thakur and Karak (2012) flushing out a new sustainable method of the reduction of graphene oxide using plant extract solutions. It might not be an overstatement to say that this work has brought some advancement towards sustainability in materials science research. Thus, the work that has established the ability of extracts from plants to achieve effective reduction of graphene oxide will open the door to the development of more research and use of green reduction processes [38].

Liu et al. (2010) describes a new approach to integrate a number of nanoparticle types by employing a universal ‘stickers Nano sheet’. By using in situ reduction, this method provides a feasible approach to the synthesis of composite nanostructures and is a potential strategy for the creation of functional nanomaterials as well. In their study Liu et al. (2010) propose a major innovation in nanomaterial fabrication with the adhesive Nano sheet.

This in-situ reduction strategy allows the placement of two or more nanoparticles and a relatively easy way of synthesizing nanostructures. This research opens the doors to more studies on the synthesis and the use of multifunctional nanomaterial for technological advance field [39].

Graphene-derived materials demonstrated to be crucial for the creation of flexible and bending technologies because of their properties. The relatively high mechanical, optical, and electrical properties of these materials and the ability to functionalize easily their derivatives are the cause of great admiration. In this paper, the recent developments reporting the synthesis and uses of graphene incorporated composites are reviewed with focus on its prospectively in areas such as energy conversion, wearable devices, and clean energy storage devices. Concerning challenges experienced in the generation of these teaching tools, the paper also recommends further research directions.

The review also covers different approaches to graphene production using techniques such as, mechanical exfoliation, chemical vapor deposition (CVD) and chemical reduction. Both methods are favorable for different aspects concerning scalability, cost, and quality of produced graphene. Graphene-based composites have promising application for flexibility and bending technology in the future new material. They are well suited for numerous uses, such as wearable electronics and energy acquisition and preservation due in large to their standout characteristics and versatility. It is important to note that graphene based composites hold great promise in contributing to the creativity and evolution of the subsequent generations of flexible electronics devices that face present challenges and benefit from constituent science advances.

The review paper of composites flexible using graphene, GO, and rGO by Razaq, et al. was a comprehensive paper that presents the development of those products. The synthesis methods, enhanced characteristics and multifunctional character of these materials determine their capacity to contribute to the development of flexible electronics. The mentioned challenges will have to be addressed for the future growth and commercialization of these high-performance composites.

The study comes up with a green synthesis method, which is bioinspired to produce silver nanoparticles (Ag NPs). Silver metal NPs were anchored via Menthapulegium flower extract on reduced graphene oxide (rGO). This technique employs the constituents of floral extract to reduce both the GO to rGO and the Ag^+ ions to Ag NPs. The reduction of GO to rGO: GO is first reduced to rGO. In situ Reduction of Ag^+ Ions: Menthapulegium flower extract obtained by the process of ultrasonication is a pool of natural reductants to convert Ag^+ ions to Ag NPs.

In particular, green synthesis approach, adopted in this study minimizes the use of hazardous materials and reagents. However, the synthesis method followed for the preparation of rGO/Ag NPs does not use any hazardous reducing agents and thus has environmental friendly nature. The process includes the reduction of graphene oxide (GO) and the formation of Ag NPs, which occurs here through reduction of the deposited silver ions on the rGO surface. Menthapulegium flower extract was used in viability of Ag NPs immobilized on rGO through the bioinspired green synthesis route because synthesis of nanomaterials is one among the efficient and sustainable methods. The produced rGO/Ag NPs nanocomposite could be well applied in environmental remediation as it not only possessed high catalytic performance for degrading organic dyes but also possessed excellent robustness and reusability [40].

As a result, it has attracted alot of attention in synthesizing reduced graphene oxide(rGO) from agro- industrial waste. This paper focuses on the characterization of rGO's physicochemical nature and its eco-friendly preparation from bio waste materials, perspectives of use in water treatment industry and pharmaceuticals.

Particle Size and Morphology: rGO is apt to operate well in several applications since it exhibits uniform particle size and morphology that are acceptable. It also has optimum particle size which provides the basis for its application in drug delivery and pollutants' identification.

Optical Properties: The optical property of rGO is good, the photocatalysis and optoelectric devices are good applications of rGO. Optically, they can be tailored by such factors as the synthesis method, as well as the extent of reduction.

Electrical Conductivity: However, rGO is much more conductive than GO, and this characteristic can be utilized for enhancing the electronic and sensing properties. Reduced rGO and the extent of oxygen-containing functional groups' removal influences conductivity.

The green synthesis of rGO is relatively a novel area of research that has recently gained a lot of attention to deal only with cost effective and eco-friendly techniques. Green methods incorporate and convert agricultural waste and other industrial wastes into materials that are used in the production process thus cutting on environmental pollution and ensures availability of raw material which is inexhaustive. The preparation of rGO by biofactory means entail the utilization of biological precursors in the preparation of rGO from GO.

They do not involve the use of toxic chemicals as in conventional reduction methods; they are environmentally friendly, and relatively cheap. Green synthesis of rGO recognizes a new area of research that embraces cost effective and environmentally friendly techniques for preparation of rGO. Green techniques incorporate agro-industrial waste materials which reduces their impact on the environment and provide countries with a sustainable source of raw material. Biofabrication of rGO involves reducing graphene oxide (GO) to rGO by employing bio based materials and processes. This process excludes the use of many hazardous chemicals that are employed in other reduction processes and is also economical and ecofriendly.

The idea of preparing rGO from agro-industrial waste is a green concept that meets the concept of sustainable development. Physicochemical characteristics, method of preparation, and potential uses for rGO have been described in this review with emphasis on biomedical and water treatment uses. The work also focuses on further research on how rGO as a functional and environmentally friendly material can address environmental issues [41].

Bai and Shen (2012) have done an excellent job on presenting a paper that gives a general background on the synthesis methods of graphene–inorganic nanocomposites, as well as their properties and applications. As this review elucidates, these materials have evolved considerably and for good reason: their distinctive characteristics lend themselves well to multiple applications. Graphene or graphene oxide (GO) is used when preforming inorganic matrices. This is the reason why the present approach ensures a homogeneous distribution of inorganic nanoparticles on the graphene surface. This method involves the direct addition of graphene or GO to already synthesized inorganic nanoparticles and processing of the resulting solution by several processes including separation through centrifugation, filtration or solvent precipitation.

Conductive graphene enhances the electrical features of the nanocomposites – a critical requirement for them to be utilized in electronics. Due to having better electrical conductivity, these nanocomposites are used in sensors, transistors and other electronic parts. The extensible energy density and superior charge discharge character of the graphene-inorganic nanocomposites make it possible for applications in batteries and super capacitors. Bai and Shen’s (2012) paper presents a clear and comprehensive state of the art treatment of graphene incorporated inorganic nanocomposites, which describes synthesis methods, properties and applications of such materials. Altogether, the paper fills the gap in the literature by providing readers with a gazetteer of challenges and potential developments for these novel materials [42].

CHAPTER 3

METHODOLOGY

3.1 Material

$KMnO_4$, $NaNO_3$, H_2SO_4, Deionized water, distilled water, H_2O_2, HCl were provided from Merck Co. Graphite were purchased as analytical grades.

3.2 Synthesis of 2D reduced graphene oxide

3.2.1 Synthesis of graphene oxide

In 150ml of H_2SO_4, 2g of graphite and 2g of $NaNO_3$ were dissolved and kept for stirring for 2hours on ice bath. 6g of $KMnO_4$ were added pinch by pinch and kept it on stirring for 20 to 24 hours. After that, 100ml of DI water were added drop wise. Then 20ml of H_2O_2 were added drop wise to stop the reaction. Washed the product with 10% HCl (200ml) and then with DI water (200ml). Left the nanoparticles for three days at 80°C in dry oven. GO nanoparticles were collected as a product (Figure 3.1) [43].

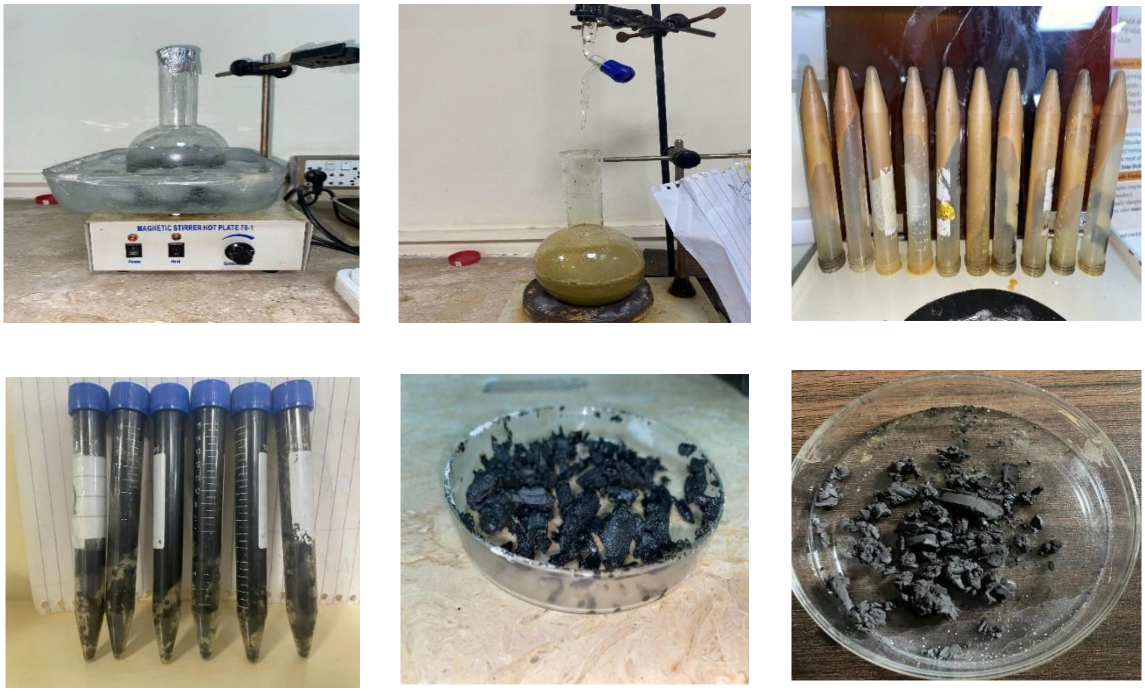


Figure 3.1 a) Reaction start b) Reaction Stop c) Centrifugation d) Partially Dried GO in falcon tubes e) Partially dried GO in petri dish f) Dried GO in petri dish

$KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^-$ (1)

$MnO_3^+ + MnO_4 \rightarrow Mn_2O_7$ (2)

$Mn_2O_7 + H_2SO_4 + C$ (graphite) $\rightarrow$ (C-O-C) $+ MnO_4 + H_2O + SO_4^{-2}$ (3)

3.2.2 Exfoliation (2D) of graphene oxide via sonication

For exfoliation 1g of GO were dissolved in 500ml of distilled water and ultra-sonication were done for 2 hours. GO centrifugation were done at 400rpm. XGO were dried at 45 °C for 2 hours (Figure 3.2) [44].

Figure 3.2 Ultra-sonication of GO

3.2.3 Reduction of graphene oxide.

To obtain rGO from GO 100mg of dried GO powder is taken in empty beaker and covered with aluminium foil with punched pores placed on a hot plate at 350 °C for 10 minutes.

3.3 Characterization techniques

For the identification of GO and rGO performed a few characterization techniques name are given in Figure 3.3. To determine the elemental composition, analysis using Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), and X-ray diffraction (XRD) was carried out. SEM was used to examine the surface morphology of the nanocomposites, and UV- vis (UV-visible) spectrometer was used to evaluate the samples' optical characteristics. XRD technique used for determination of the crystalline phases, the size and morphology of the nanocomposite, and the degree of orientation of the nanoparticles in the matrix. It was also used to check the presence of defects, and the interfacial interactions between the nanoparticles and the matrix. The chemical surface and reactive sites of the nanoparticles were investigated by using FT-IR technique.

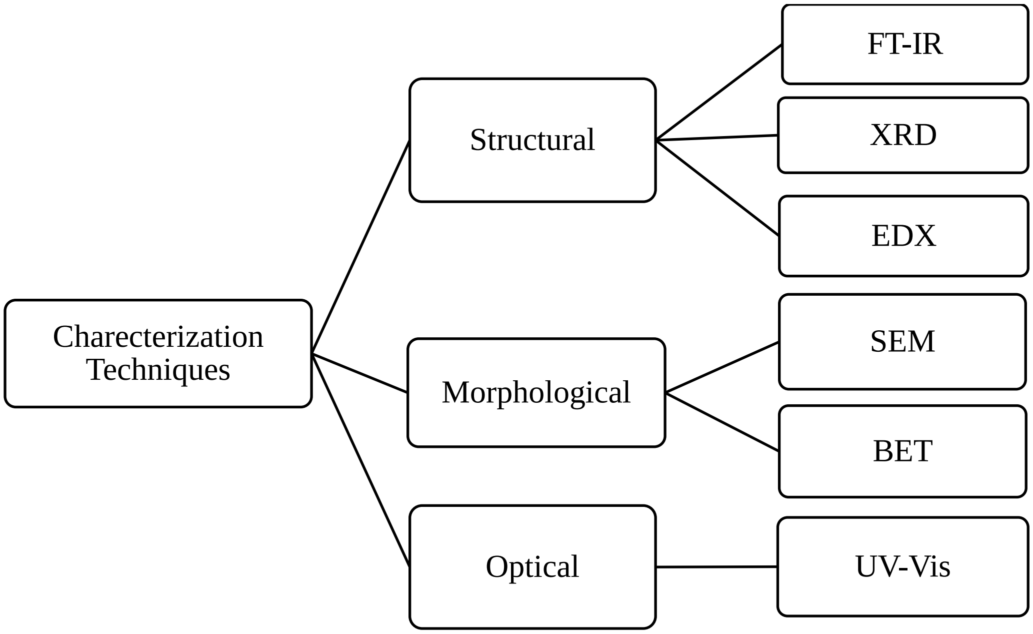


Figure 3.3 Summary of characterization done in this research.

3.4 Photocatalytic activity procedure

For this purpose, 0.5g of photocatalyst was dissolved in 80mL of water, acting as a reducing agent that can supply electrons for reduction. The photocatalytic photoreactor was purged using a pressure of 30 Psi. The catalyst surface was kept 5 cm from the illumination, which was evenly distributed across the reactor walls and intensified by about 3.5729 W/cm^2 [45]. The liquid samples were collected over the course of one hour, and the reaction lasted for roughly four hours. Hourly liquid samples were loaded into a GC-FID (Agilent 6890N with Head-space Sampler G1888, USA) for analysis using a DB-Wax Column and a stationary phase of polyethylene glycol. Nitrogen, which was 99.995% pure, was the carrier gas utilized for analysis [46]. To ascertain the unknown content of the final product and the detector's linear response to a specific component, the calibration curve for various possible product such as methanol at various concentrations was plotted. Methanol's Minimum Detection Limit (MDL) was determined to be 25 ppm, indicating the lowest response value that could be identified [47].

CHAPTER 4

RESULTS

4.1 Structural techniques

4.1.1 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectrum was acquired, both the GO and XrGO spectra that were produced revealed that the graphite had been successfully oxidized (Figure 4.1). The O-H stretching vibration is responsible for the broad and powerful absorption peak located at 3390 cm^{-1}. The C=O stretching of the carboxyl group is liable for the peaks at about 1730 cm^{-1} and 1717 cm^{-1}, the C=C stretches from the unoxidized graphitic domain are responsible for 1619 cm^{-1} and 1595 cm^{-1}, the C–O stretching bond is relevant for 1377 cm^{-1}, and the vibration modes of the epoxide (C–O–C) are significant for 1316 cm^{-1} and 1230 cm^{-1}. The peak at about 1143 cm^{-1} is ascribed to the epoxy group's C=O stretching vibration, 1062 cm^{-1} to the C-O-H vibration mode, 1020 cm^{-1} to the existence of the alkoxy group's C-O starching vibration, 950 cm^{-1} and 850 cm^{-1} to the epoxy group's compliance with the deformation vibrations. GO and XrGO functional group with reference are mention in the table 4.1.

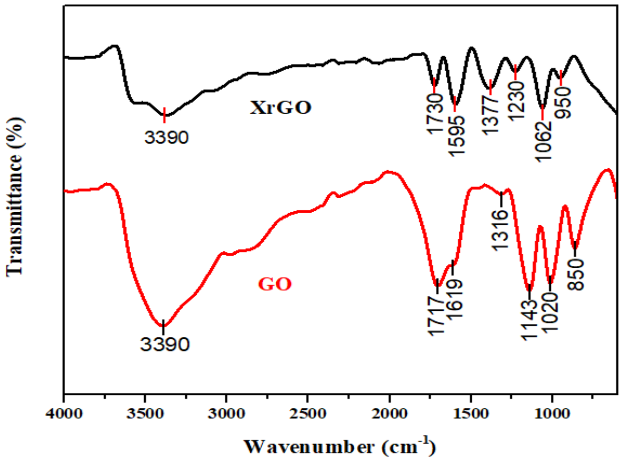


Figure 4.1 Comparative FT-IR spectra of GO and XrGO

Table 4.1 Wavenumber with functional group FT-IR spectra.

GO and XrGO		
Wavenumber (cm^{-1})	**Functional group**	**References**
3390	O-H	[48]
1650-1750	Carboxyl group stretching (-COOH)	[49, 50]
1580-1619	C=C stretch	[49-51]
1377	C-O stretching	[50]
1230-1320	Epoxide (C-O-C)	[49]
1143	Epoxy group (C=O)	[52]
1062	C-O-H	[50]
1020	Alkoxy group (C-O)	[53]
850-960	Epoxy or peroxide group (C-O)	[53], [48]

4.1.2 X-ray diffraction (XRD)

The phase structures of unmodified GO and XrGO was examined by X-ray diffraction (XRD) measurement (Figure 4.2). The main reflex of GO appears at 38° corresponding to the interplanar distance between the graphene sheets equal to 2.3 nm. The diffraction peak of XrGO is located at 39° with an interlayer distance of 2.2 nm, revealing that many different oxygen-containing groups were intercalated within the interlayer space [54].

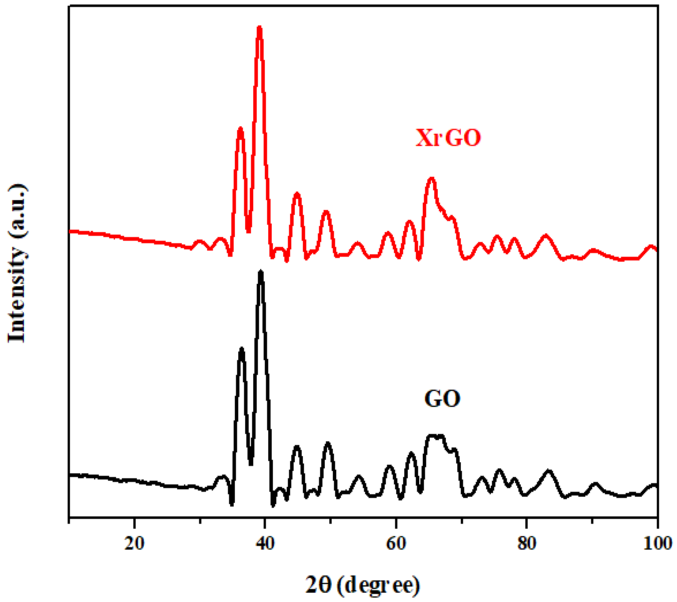


Figure 4.2 XRD measurement of GO and XrGO

4.1.3 Energy-dispersive X-ray spectroscopy (EDX)

Carbon, oxygen, sulphur, manganese, potassium, and iron are all confirmed by the EDX spectra of XrGO, which is displayed in Figure 4.3. However, throughout the reduction process, iron, manganese, and potassium were present as impurities. Table 4.2 provides a summary of XrGO's chemical makeup. The hydrazine hydrate was lowered from GO to XrGO, as seen by the decreasing oxygen content in XrGO [55].

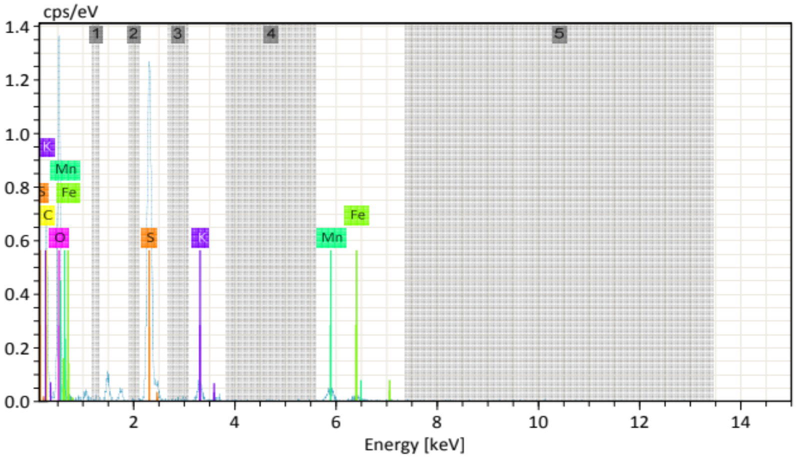


Figure 4.3 EDX spectra of XrGO.

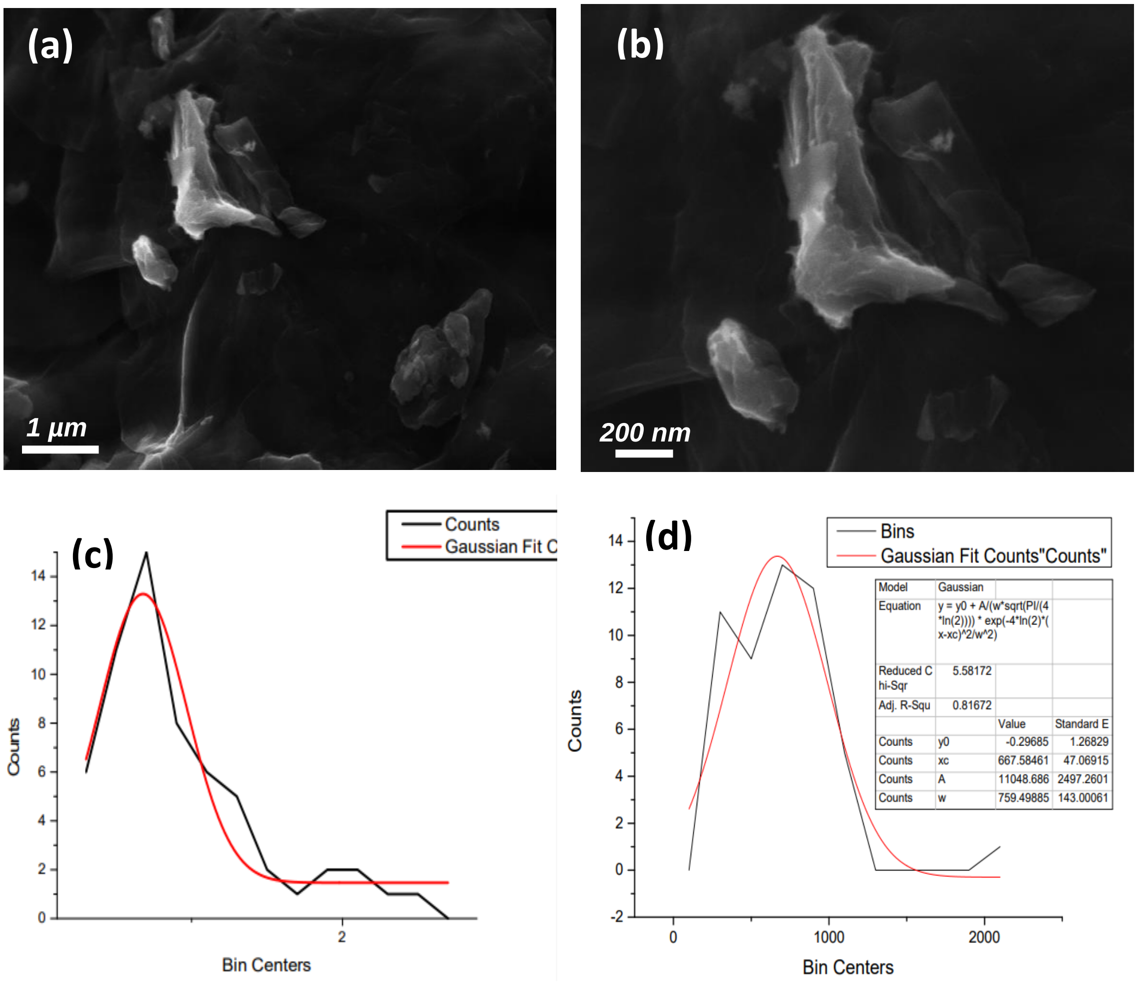
Table 4.2 EDX analysis results.

Element	**Mass (%)**	**Mass Norm. (%)**	**Atom (%)**
Oxygen	43.52	45.32	46.45
Carbon	30.69	31.96	43.44
Sulfur	15.32	15.96	8.12
Manganese	3.71	3.86	1.15
Potassium	1.45	1.51	0.63
Iron	1.43	1.40	0.41
Sum	**96.04**	**100.00**	**100.00**

4.2 Morphological techniques

4.2.1 Scanning electron microscopy (SEM) of GO

Figure 4.4 (a, b) displays the SEM pictures of the GO nanosheets that were synthesized and functionalized using the Hummer's technique. The pictures depict a two-dimensional graphene oxide structure that is stacked and wrinkled like a sheet. The pictures show the separation between the layers and the thin edges. The structure of oxidized graphene resembles a thin screen, and its sheets are comparatively big. The surface of functionalized GO shows a relatively higher degree of roughness than the GO [56]. The average thickness of 2D sheets of GO calculated as shown in the figure 4.4 (c), and (d).

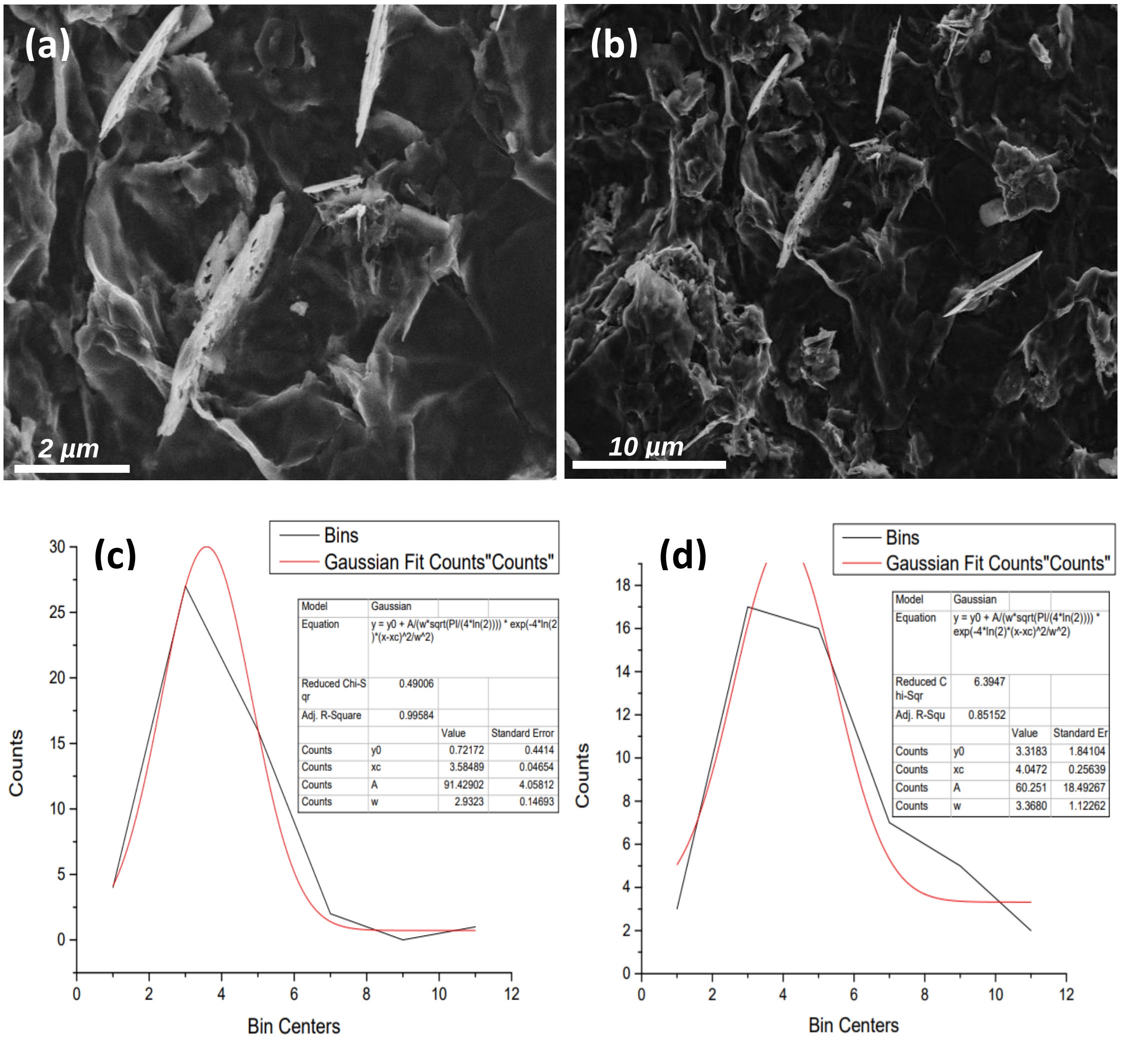


Model	Gaussian		
Equation	y = y0 + A/(w*sqrt(PI/(4*ln(2)))) * exp(-4*ln(2)*(x-xc)^2/w^2)		
Reduced Chi-Sqr	5.58172		
Adj. R-Squ	0.81672		
		Value	Standard E
Counts	y0	-0.29685	1.26829
Counts	xc	667.58461	47.06915
Counts	A	11048.686	2497.2601
Counts	w	759.49885	143.00061

Figure 4.4 Scanning electron microscopy images of graphene oxide (a), (b), and average thickness of 2D sheets of GO (c), (d).

SEM of XrGO

The produced XrGO appears as tiny, flaky particles (Figure 4.5 (a, b)). More noticeable creases are the result of the XrGO structure. It has been asserted that XrGO sheets' wrinkled form enhances their overall capability for charge accumulation [57]. The average thickness of 2D sheets of XrGO calculated as shown in the figure 4.5 (c), and (d).



Model	Gaussian		
Equation	y = y0 + A/(w*sqrt(PI/(4*ln(2)))) * exp(-4*ln(2)*(x-xc)^2/w^2)		
Reduced Chi-Sqr	0.49006		
Adj. R-Square	0.99584		
		Value	Standard Error
Counts	y0	0.72172	0.4414
Counts	xc	3.58489	0.04654
Counts	A	91.42902	4.05812
Counts	w	2.9323	0.14693

Model	Gaussian		
Equation	y = y0 + A/(w*sqrt(PI/(4*ln(2)))) * exp(-4*ln(2)*(x-xc)^2/w^2)		
Reduced Chi-Sqr	6.3947		
Adj. R-Squ	0.85152		
		Value	Standard Er
Counts	y0	3.3183	1.84104
Counts	xc	4.0472	0.25639
Counts	A	60.251	18.49267
Counts	w	3.3680	1.12262

Figure 4.5 Scanning electron microscopy images of exfoliated reduced graphene oxide at (a), (b), and average thickness of 2D sheets of XrGO (c), (d).

4.2.2 X-ray photoelectron spectroscopy (XPS)

Carbon, oxygen, iron, and copper are all present in the GO XPS spectra (Figure 4.6 (a)). Additionally, the C/O ratios of GO (C/O 2.3) show that the sp^2 carbon domain has been restored and that oxygen clouds have significantly decreased. Gaussian functions for GO were used to numerically fit the electronic 1s core levels of C. The binding energy configurations found in the C 1s region of GO (Figure 4.6 (b)) is 285.29 sp^3 groups [58].

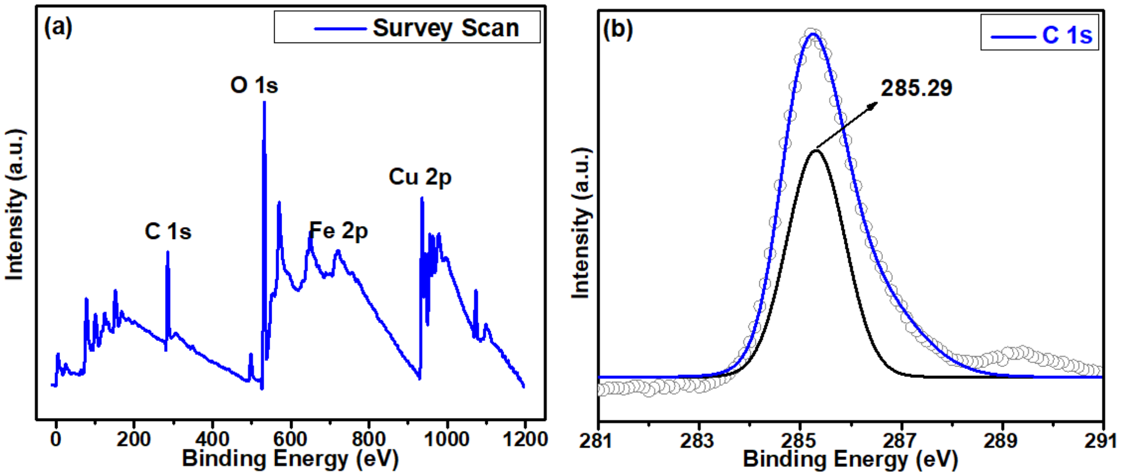


Figure 4.6 (a) XPS spectra of GO in C 1s, O 1s, Fe 2p, and Cu 2p region (b) XPS spectra of GO in C 1s region.

4.3 Optical technique

4.3.1 UV-Vis spectroscopy

The UV-Vis spectroscopy is a non-destructive analysis (Figure 4.7). The π → π* transition of aromatic C–C bonds and the n → π* transition of C=O are responsible for the two maximum bands in the UV-vis spectra of GO, which were observed at 225 and 300 nm (Table 4.3). The peak of exfoliated reduced graphene oxide was detected at 240 nm following reduction by ascorbic acid [51] [59].

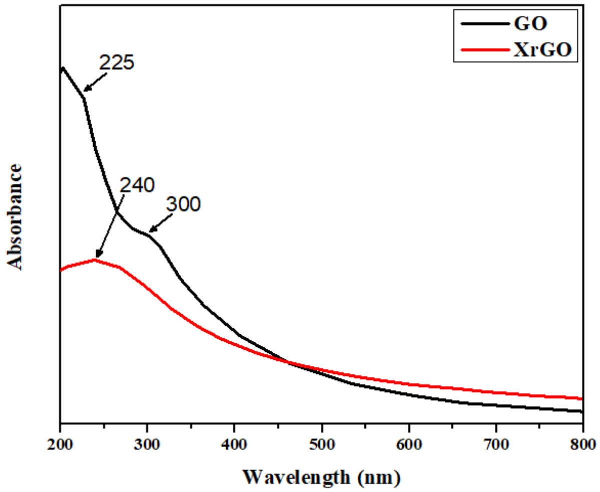


Figure 4.7 UV-Vis spectra of GO and XrGO

Table 4.3 Wavelength with transition UV-Vis spectra.

Nanomaterials	**Wavelength (nm)**	**Transition type of π**	**Bandgap energy (eV)**
GO	225	π-π*	3.56
	300	n-π*	
XrGO	240	π-π*	3.44

Band Gap:

The Wood and Tauc plot equation is used to determine the band gap of GO and XrGO [60] are given below

$$\alpha h\nu = k(h\nu - Eg)^n \quad (1)$$

Here, α is the absorption coefficient, which was calculated using the provided formula

$$\alpha = 4\pi k/\lambda \quad (2)$$

Here, λ stands for wavelength and k for absorbance.

The E_g values of 3.56 eV and 3.44 eV for GO and XrGO, respectively (Figure 4.8), confirming that the two produced graphene-based nanomaterials are wide bandgap semiconductors with E_g values between 3 and 5 eV [61]. The table lists the variations in the π transition types and Eg values for each of the generated graphene-based nanomaterials.

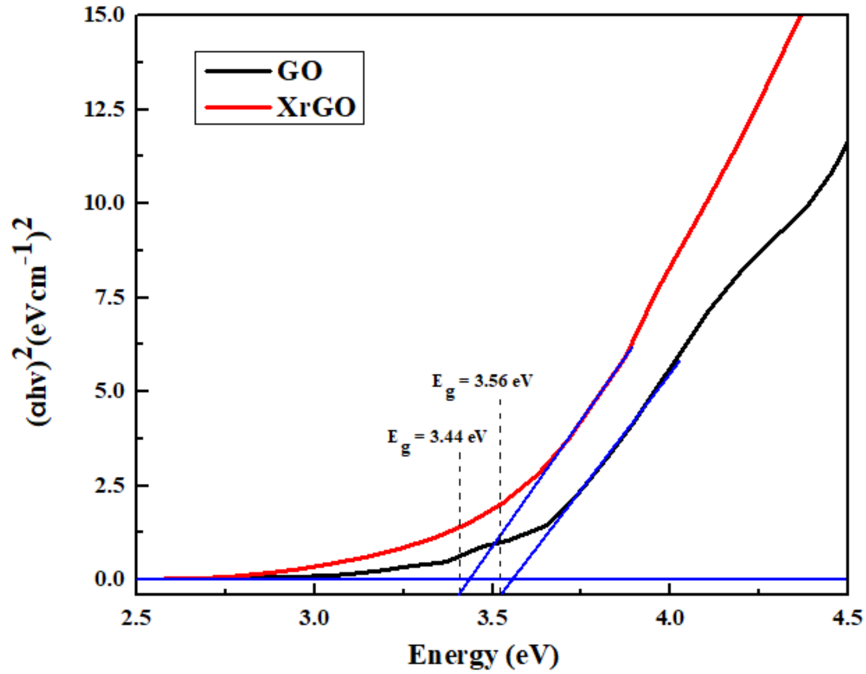


Figure 4.8 Bandgap of GO and XrGO

4.3.2 Photoluminescence (PL)

Figure 4.9 shows the PL spectra of the GO and XrGO publications. Graphite is a semiconductor material that lacks luminescence and has a zero band gap. However, the quantum effect will cause the band gap to expand when its size is reduced to the nanoscale. Carbon vacancies and oxide functional groups in GO and XrGO sheets will cut the graphene to create a nano-carbon cluster, giving them semiconductor characteristics and causing luminescence. The recombination of electron-hole pairs in the local state of the sp^2 carbon cluster contained in the sp^3 matrix is responsible for the three emission peaks shown in the GO article, which are positioned at 560, 578, and 608 nm, respectively. The PL intensity of XrGO drops very quickly as compared to GO paper. Blue shift is visible at the peak at 578 nm. Oxide functional groups shrink and the sp^2 carbon cluster enlarges as GO is lowered. PL emissions rapidly diminish or perhaps vanish as GO transforms into graphene structures [62].

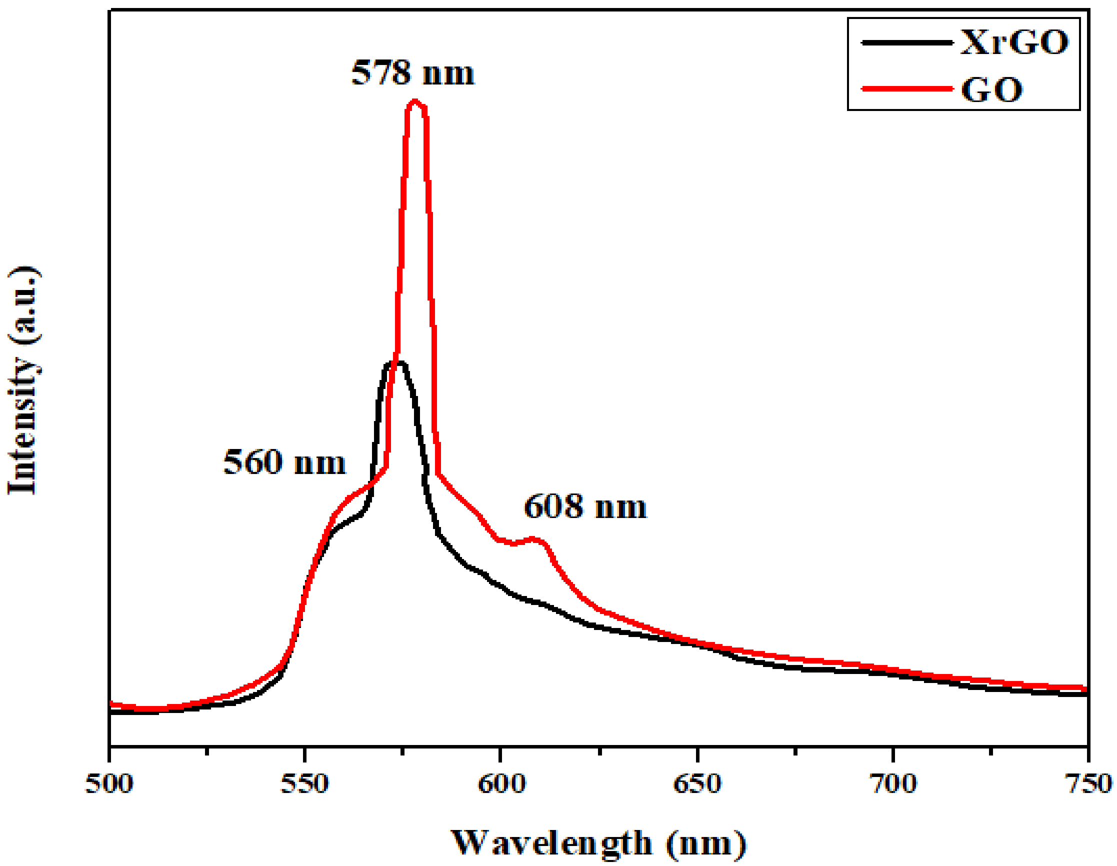


Figure 4.9 PL spectra of GO and XrGO.

4.4 Photocatalytic activity/ performance

We conducted a number of control tests, such as 1) one in which carbon dioxide was not passed into the photocatalytic reactor, to make sure that the synthesis of methanol would result from the photocatalytic reduction of carbon dioxide, 2) Without a light source (both visible and ultraviolet), 3) The photocatalyst put onto the reactor is not available and 4) Without the reducing agent of water. In such an experiment, there are no products to detect because they must come from the pollutants rather than the CO_2 [63]. The amount of product found in the real CO_2 reduction is modified by the amount in the blank operation if product formation is recognized in order to prevent an overestimation of product production [64]. Methanol formation occur when all conditions were provided (Table 4.4).

Table 4.4 Elucidates sundry control experiment to affirm the source of carbon-based compounds, X = Without particular substance, ☑ = Sign shows availability of particular reactants

Experiment No	Reaction Conditions				Methanol Formulation
	CO_2	Light Intensity	Photocatalyst	Reducing Agent	
1	X	☑	☑	☑	X
2	☑	X	☑	☑	X
3	☑	☑	X	☑	X
4	☑	☑	☑	X	X
5	☑	☑	☑	☑	☑

In order to achieve this, 0.5g of photocatalyst was dissolved in 80mL of water, acting as a reducing agent that can supply electrons to enable reduction. With pressure ranging from 30 Psi, the photocatalytic photoreactor was purged at a steady flow rate of 0.15 mL/min. The catalyst surface was kept 5 cm from the illumination, and the light was evenly distributed throughout the reactor walls with an intensity of about 3.5729 W/cm^2 [45]. For each composition of the photocatalytic nanocomposite, the liquid samples were taken over a period of one hour, and the reaction was carried out for approximately five hours. Hourly liquid samples were loaded into a GC-FID (Agilent 6890N with Head-space Sampler G1888, USA) for analysis using a DB-Wax Column and a stationary phase of polyethylene glycol. Nitrogen was the carrier gas utilized for the analysis (99.995% pure) [65]. We only looked at the creation of liquid products in these studies; we did not look into the possibilities of detecting gaseous compounds like CO, CH_4, H_2, etc. To ascertain the unknown content of the final product and the detector's linear response to a specific component, the calibration curve for methanol at various concentrations was plotted. Methanol's Minimum Detection Limit (MDL) was determined to be 25 mg/mL, indicating the lowest response value that could be found [66].

4.5 Photocatalytic CO_2 reduction performance

The methanol yield for GO, rGO, XGO, and XrGO was shown as a function of time to determine the photocatalytic activity for the synthesis of solar fuels. The methanol yield for photocatalysts was displayed in the table, with XrGO having the greatest yield (0.26 mmol $g^{-1}h^{-1}$) in comparison to GO, rGO, and XGO, which were found to be approximately 0.101, 0.143, and 0.053 mmol g^{-1} h^{-1} for GO, rGO, and XGO, respectively. Rapid charge carrier recombination and reduced electron transfer are the causes of the lowest GO yield. Because of the large quantity of oxygen atoms in the electronic structure of GO, there is a defect that prevents electrons from flowing freely, which lowers the quantum efficiency (Table 4.5) [67].

The rate of methanol Yield was calculated by using the following formula [17];

$$Yield = \frac{Con. of\ product\ (ppm)\ \times\ Volume\ of\ Solution\ (L)}{Mass\ of\ photocatalyst\ (g)\ \times\ Reaction\ time\ (Hours)}$$

The Quantum Efficiency or Yield can be estimated from the given expression [46]

$$QE = \frac{No. of\ \ moles\ of\ product\ formed\ \times\ No. of\ e^{-1}\ required}{No. of\ Photons\ absorbed\ by\ \ photocatalyst}\ x\ 100$$

$$QE = \frac{No. of\ \ moles\ in\ mol\ l^{-1}\ *\ 6\ *\ NA}{IE\ \times\ A\ \times\ \lambda\ \times \mathrm{T}\ \times h\ \times C}$$

where IE stands for light intensity (3.5729 W/cm^2), A for photocatalyst irradiated area (0.00321 m^2), λ for bombarded wavelength of light (>400 nm for visible light), h for plank's constant (6.634 × 10-34 J.s), C for speed of light (3 × 108 $m.s^{-1}$), T for reaction time in seconds (3600 s), and NA for Avogadro's number (6.02 × 1023).

Table 4.5 Photoreduction of CO_2 into methanol under certain controlled experimental conditions

Sample	**Reaction Precursor**	**Reducing Agent**	**Visible/UV Light (nm)**	**Time (hour)**	**Methanol Yield (mmol/gh)**	**Quantum Efficiency$_{max}$ (%)**
GO	Co_2	H_2O	400/265	4	0.101	1E-4
XrGO	Co_2	H_2O	400/265	4	0.26	2.8E-4
rGO	Co_2	H_2O	400/265	4	0.143	1.5E-4
XGO	Co_2	H_2O	400/265	4	0.053	5E-5

GO, rGO, and XGO results were no sharp peak of any organic fuel only diluent behavior was observed. In XrGO sharp peak was observed at 6 mints that was related to standard sample running parallel and that sharp peak was peak of methanol (Figure 4.10).

$$GO_{VB} + hv \longrightarrow GO_{VB} + h^{+} + e^{-} \qquad (3)$$

$$h^{+} + H_2O \longrightarrow 1/2O_2 + 2H^{+} \qquad (4)$$

$$GO_{CB}\text{----}CO_2 + e^{-} + H^{+} \longrightarrow CH_3OH \qquad (5)$$

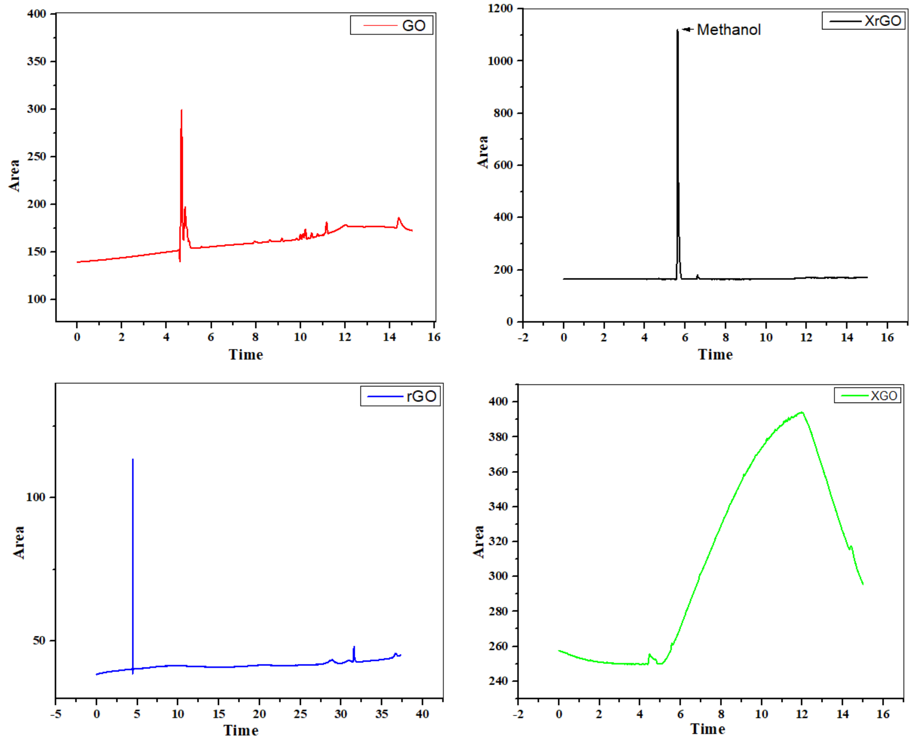


Figure 4.10 GC-FID results of photocatalytic activity.

4.6 Effect of Pressure on CO_2 photoreduction

For the purpose of photocatalytically converting carbon dioxide into methanol, the CO_2 pressure was raised from 30 kPa to 180 kPa. According to the graph, the photoreduction of carbon dioxide increased up to about 90 kPa. This could be because the concentration of carbon dioxide in the photocatalytic system increased, making it easier for the carbon dioxide to be converted into solar fuels like methanol and formic acid. As the pressure increases, more carbon dioxide enters the reaction system and diffuses more readily to the catalyst surface's reactive active sites. In order to prevent catalyst poisoning, the increased pressure also prevents backward reduction reactions from taking place on the catalyst surfaces. As seen in the figure, the decrease in production rate (mmol/gh) and quantum efficiency (%) was noted above 90 kPa and up to 180 kPa (Figure 4.11). This could be attributed to the occupancy factor of reactive active sites by unstable and ineffective byproduct molecules, which inhibited the adsorption of carbon dioxide. It can be inferred that the absorption of carbon dioxide would need to occur at the optimal pressure ($P_{optimum}$) in order for it to be converted into methanol.

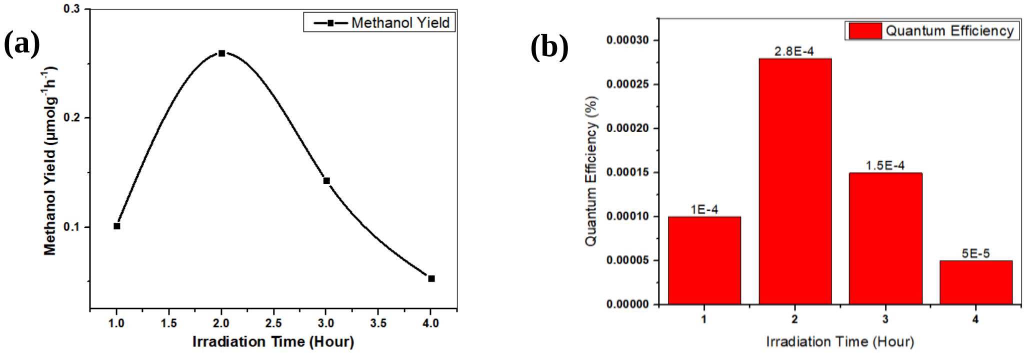


Figure 4.11 Photocatalytic CO_2 reduction (a) Methanol yield, and (b) quantum efficiency

4.7 Product formation (Methanol) mechanism

The process of photocatalyst CO_2 is pumped from a cylinder to the photoreactor, which consists of a sealed system with water and catalyst suspended by mixing on a magnetic stirrer. UV or Visible light lamps face the reactor. A GC-FID analysis is used to take methanol measurements (Figure 4.12).

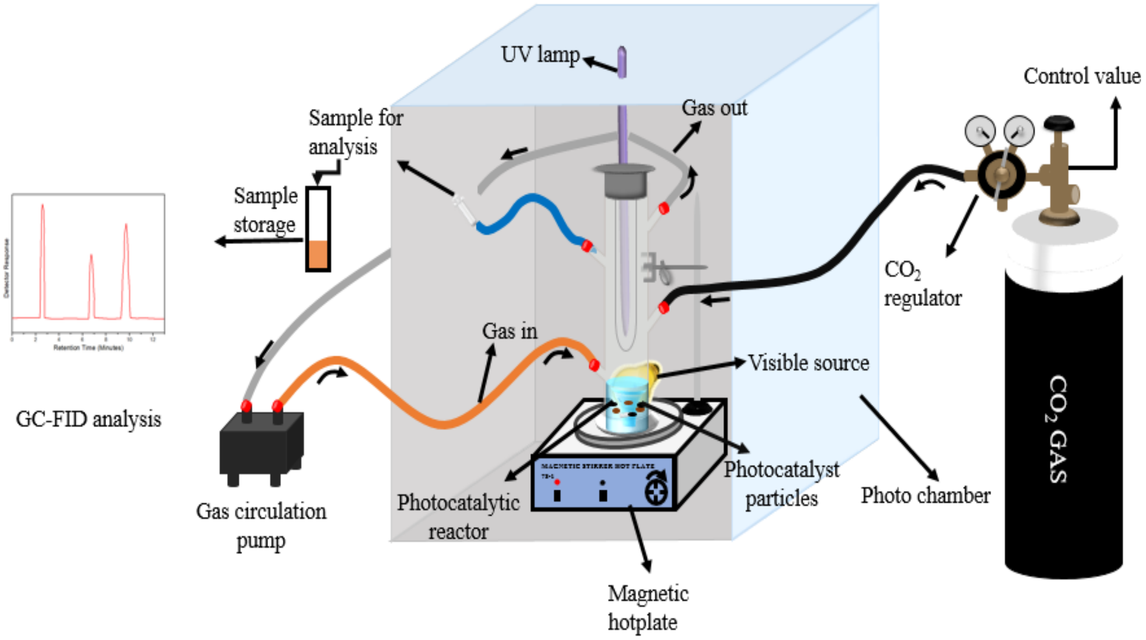


Figure 4.12 Photocatalysis of CO_2 reduction

XrGO nanoparticles produce electron-hole pairs and efficiently absorb visible light. The photogenerated electron in XrGO conduction band can readily migrate to rGO nanosheets, preventing electron-hole pair recombination and facilitating electron transport to the catalytic sites for CO_2 reduction. The XrGO is more likely to absorb CO_2 if it has a wide surface area and multiple faulty spots. XrGO photogenerated electrons decrease the CO_2 that has been absorbed into methanol. Protons (H^+) were eventually produced when the water molecules were oxidized by photogenerated holes. As seen in Figure 4.13, six moles of photo-generated electrons interacted with one mole of CO_2 and six moles of H^+ to decrease them. As a result, 1.5 moles of oxygen and one mol of methanol should be produced. The mole ratio of oxygen to photogenerated methanol, or 1:1.3, provided more evidence for this.

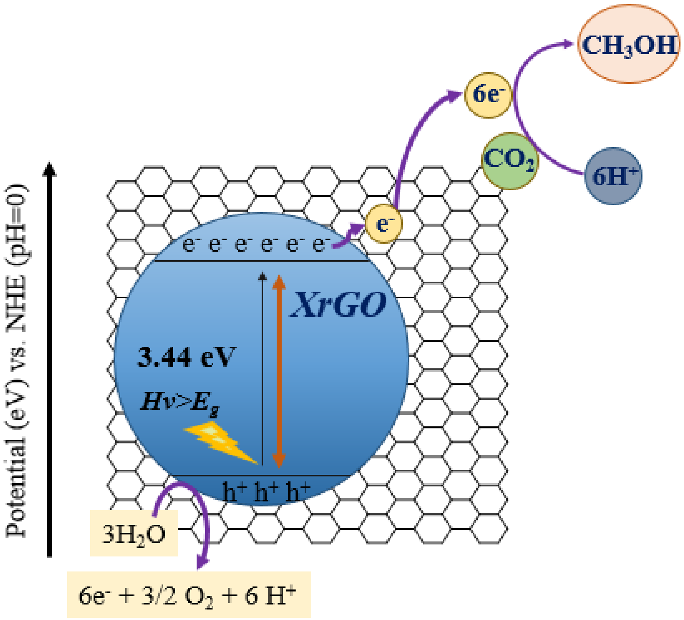


Figure 4.13 Methanol formation with CO_2 reduction

CHAPTER 5

DISCUSSION

The photocatalytic CO_2 reduction test has been conducted by a number of research teams to examine graphene oxide's capacity for photocatalytic CO_2 reduction. Graphene oxide (GO) has been shown by Hsu and colleagues to be an effective photocatalyst for the reduction of CO_2. Specifically, a modified Hummer's approach was used to prepare the GO. GO, XrGO, rGO, and XGO are the names of the four samples that were created. The prepared GO, XrGO, rGO, and XGO samples possessed band gap values of roughly 3.56 and 3.44 eV, respectively, and lacked strong absorption edges. A test for gas phase photocatalytic CO_2 reduction was conducted. According to the findings, rGO and XrGO can be adjusted and modified to function as efficient solar energy harvesting materials. Overall, graphene has been regarded as a potential material for photocatalytic CO_2 reduction due to its exceptional qualities, which include high conductivity, huge surface area, outstanding flexibility and stability, and single-layer structure. In addition to increasing the photocatalytic CO_2 reduction activity, graphene-based photocatalysts can also give them a number of novel and special synergistic qualities. To achieve the actual use of graphene-based photocatalyst for CO_2 reduction to solar fuels, however, a number of theoretical and fundamental problems need to be addressed and given further consideration. First, a thorough examination of the photogenerated charge carriers' migration path between the semiconductor and the XrGO is necessary. By acting as an electron acceptor, XrGO can efficiently lower the semiconductor's electron–hole recombination rate, increasing the photocatalytic CO_2 reduction activity. However, the results of the photocatalytic reaction and indirect characterization, like the photocurrent response test, led to this conclusion and inference. In order to clearly examine the migration path of the photogenerated charge carriers on the photocatalyst/graphene interface and the variations in the number of the photogenerated charge carriers during the photocatalytic reaction, the superior electron conductivity of XrGO should be further investigated using more potent characterization tools, such as UV-Vis, XPS, EDX, PL, and GC-FID. Second, it is yet unknown how XrGO affects product production during photocatalytic CO_2 reduction; this needs to be thoroughly investigated. Using an XrGO-based photocatalyst, a variety of products, including CH_4, HCO_2H, CH_2O, and CH_3OH, may be identified following photocatalytic CO_2 reduction. The generation of the various products during the photocatalytic CO_2 reduction reaction was discovered to be influenced by the presence of graphene. Third, in order to manufacture high-quality graphene nanosheets for photocatalytic CO_2 applications, graphene modification and optimization should constantly be considered. Fourth, more focus should be placed on how stable graphene-based photocatalysts are against photo-corrosion during photocatalytic reactions. According to a recent study by Kamat et al., graphene can mineralize into H_2O and CO_2 as a result of the $OH^{\bullet}$ radical attacking it during the photocatalytic event. To put it briefly, it has been demonstrated that photocatalytic CO_2 reduction to create solar fuels utilizing solar energy is a viable tactic for lowering the amount of CO_2 in the atmosphere and creating a sustainable energy source.

Light absorption ability, photogenerated charge carrier separation efficiency, CO_2 absorption capability, CO_2 activation capability, and surface reactant kinetics are the five factors that affect the photocatalytic CO_2 reduction activity. This viewpoint shows that by enhancing these five factors, XrGO-based photocatalysts provide a wealth of options for the photocatalytic CO_2 reduction area.

The results of the study align with various aspects of the existing literature on graphene oxide and exfoliated reduced graphene oxide, particularly in relation to their application in CO_2. With a yield of 0.26 mmol g^{-1} h^{-1}, the XrGO results for the photocatalytic reduction of CO_2. Since XrGO is known to enhance photocatalysis by inhibiting electron-hole pair recombination, both materials should have comparable photocatalytic efficiency, per published research. The increased photocatalytic effectiveness of XrGO may be explained by its superior ability to absorb light and generate reactive oxygen species for CO_2 reduction.

CONCLUSIONS / RECOMMENDATIONS

GO was successfully reduced to exfoliated XrGO by employing ultra-sonication as an effective method. This method's merits include its scalability and the removal of functional groups from GO. When exposed to visible light, the photocatalytic reduction of CO_2 to methanol showed that XrGO exhibited the highest yield. Furthermore, the synthesized XrGO demonstrated good recyclability. The GO and XrGO surfaces are clearly visible in SEM pictures. A quantitative analysis of the XrGO elemental composition is conducted using EDX in conjunction with SEM morphology. The XrGO produced a roughly six-fold increase in methanol output and a considerable increase in photocatalytic efficiency. The effective charge transfer of photogenerated electrons via the XrGO skeleton and the slow recombination of charge carriers were credited with the enhanced photocatalytic activity. Furthermore, there is a lot of promise for the sustainable conversion of CO_2 into useful compounds with the aid of visible light when metal oxide catalysts are widely accessible and reasonably priced.

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